EXPERIMENTAL CHEMISTRY

FOR

JUNIOR STUDENTS

BY

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PART IV.

CHEMISTRY OF CARBON COMPOUNDS
OR ORGANIC CHEMISTRY.

(*With an Appendix on Ultimate Organic Analysis.*)

PREFACE.

THIS volume completes the author's course of Experimental Chemistry and provides the student with a practical as well as theoretical introduction to the great Organic division of the Science.

Much care and labour have been expended in elaborating this part of the course so as to preserve the continuity of the work while seeking to harmonise the natural with the systematic study of carbon compounds. The author's aim throughout has been to help the student to acquire a sound knowledge of the prominent facts and principles of the Science without overburthening him by undue detail. On the other hand much space has been devoted to the examination of such analytic and synthetic operations as throw light on the structure of organic substances. This kind of inquiry is a source of keen intellectual pleasure to thoughtful students, and is of high educational value when legitimately pursued. The best corrective of hard mechanical conceptions of molecular structure is the study of the chemical changes that can be

induced by variations of experimental conditions, and such guards the writer endeavours to provide.

It is to be regretted that no cheap and full work of reference is to be had in English corresponding to Beilstein's excellent 'Handbuch der organischen Chemie.' That work gives copious references to original memoirs, and, being kept well up to date, is one which can be strongly recommended to those who are acquainted with the German language.

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EXPERIMENTAL CHEMISTRY

JUNIOR STUDENTS.

PART IV.—ORGANIC.

CHAPTER XLVI.

INTRODUCTORY—DESTRUCTIVE DISTILLATION OF
WOOD—WOOD SPIRIT, OR METHYL ALCOHOL.

THE reader has already learned, in the course of our
experimental inquiry, that green plants absorb carbon
dioxide from the air and decompose it in the chloro-
phyll cells under the influence of sunlight.[1] The
oxygen of the dioxide is, for the most part, returned
to the atmosphere, but the carbon is retained and
assimilated along with the elements of water. Bota-
nists find that the first recognisable product of this
assimilation is the distinct chemical compound *starch*,
and that this starch is, generally speaking, the material
from which most other compounds are derived that
form the plant-structure. Ammonia and mineral
matter drawn from the soil supply the nitrogen and
other elements necessary for the production of some

[1] See Experiment 91, Part II.

of these bodies, but in several instances starch alone affords the new substances.

One of the most important of these products of the transformation of starch is the body named *cellulose.* This is the material of which the cell-walls of the plant consist, and by which its *woody tissue* is built up—in fact ordinary wood is somewhat impure cellulose.[1]

The interesting question of the relative composition of starch and cellulose now arises, and analysis can alone supply the answer.

Each body is found to consist of carbon, hydrogen, and oxygen, and of these elements only. The percentage composition of the purest obtainable specimens proved to be--

			Starch	Cellulose
Carbon	.	.	44·44	44·45
Hydrogen	.	.	6·17	6·17
Oxygen	.	.	49·39	49·38
			100·00	100·00

The two series of numbers are practically identical, as the minute differences are doubtless due to un-avoidable errors in analysis. We thus arrive at the remarkable conclusion that these two chief products of the assimilation of carbon by plants—which we well know to be perfectly distinct in general properties—consist of the same elements combined in the *same proportions.* They are therefore *isomeric compounds.*[2]

It is admitted that pure starch and cellulose are

----

[1] Fine filtering paper is nearly pure cellulose.

[2] Ἴσος equal, μέρος part.

true chemical compounds; we can therefore deduce their formulæ from the above analyses by the usual method already described in Chapter VII. Part I. When the analytical numbers obtained from starch are divided by the respective atomic weights, we get the following quotients :—

$$\text{C} \quad . \quad 44\cdot44 \div 12 = 3\cdot70 = 1\cdot201 = 6\cdot005$$
$$\text{H} \quad . \quad 6\cdot17 \div 1 = 6\cdot17 = 2\cdot003 = 10\cdot015$$
$$\text{O} \quad . \quad 49\cdot39 \div 16 = 3\cdot08 = 1\cdot000 = 5\cdot000$$

We thus arrive at the formula

$$C_6H_{10}O_5$$
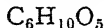
as the simplest expression for Starch.

Since the percentage composition of cellulose is the same as that of starch, its *empirical* formula must obviously be the same, but it does not follow that its *rational* formula is the same—in fact the wide difference in properties which everyone knows to exist between starch and wood-fibre is evidence that they must differ either in the mode of arrangement of the atoms within the molecules or in molecular weights.[1] Cases of *isomerism* such as this are very common in organic chemistry, and are capable of satisfactory explanation, but for the present it is sufficient to recognise the remarkable *fact* that the two very dissimilar bodies starch and wood-fibre are identical in ultimate composition and therefore are represented by the same *empirical* formula.

[1] If the molecular weights are the same, the bodies are said to be *metamers* : if the molecular weights are different, they are termed *polymers*. Thus $C_{12}H_{20}O_{10}$ is a polymer of $C_6H_{10}O_5$. Starch and cellulose are probably much more complex bodies (*see* STARCH).

The expression $C_6H_{10}O_5$ also indicates that hydrogen and oxygen are present in both compounds in the exact proportions required to form water—they thus *seem* to be hydrates of carbon or, as they are commonly termed, *carbohydrates.* As a rule these bodies are easily carbonised when brought in contact with powerful dehydrating agents ; thus when a splinter of wood or a fragment of starch is dipped in warm oil of vitriol blackening occurs, as the elements of water are removed by the acid and there remains a highly carbonised residue, or carbon itself.

It is clear, then, that carbon and water are alone necessary for the production of such bodies as starch and wood-fibre ; hence the oxygen of the air-derived carbon dioxide is not required by the plant, and most of it is returned to the atmosphere. Thus the peculiar chemical composition of the immediate products of the assimilation of carbon is an important factor in the maintenance of the proportion of oxygen in atmospheric air necessary for the support of the life of man and of the higher animals.

Viewed in the light of the facts just stated, the living plant is a laboratory in which chemical operations of the highest importance are almost constantly in progress ; on the one hand the plant purifies the air, and on the other it builds up from purely mineral matter derived from air and soil not only starch and wood-fibre but many other even more complex carbon compounds of which organised bodies are almost exclusively constructed. Thus we pass from 'Inorganic Chemistry' to that great division of the science termed 'Organic Chemistry.'

The implied distinction is, however, now one of terms rather than reality. It was supposed that chemical compounds formed under the influence of 'vital force' were a special class apart; but this distinction was shown to be an artificial one when syntheses of numbers of such bodies were effected from purely inorganic materials, and without the intervention of plant or animal organisms. It is no longer possible to recognise any real difference between the principles which govern the formation and relations of the carbon compounds which are the chief materials or products of organised bodies, and those which operate in purely inorganic nature; hence the term 'Organic Chemistry' has no longer its old and restricted meaning, but may now be defined as 'the chemistry of carbon compounds.'

In commencing our course of experimental Organic Chemistry, we shall follow the natural order of study indicated by the foregoing observations, and use in our earlier operations the chief products of the assimilation of carbon by plants, namely, wood-fibre and starch. From both bodies products can be obtained which are of great practical importance. Experiment 217 (Part II.) has already made us acquainted with several of the changes observed when wood is subjected to *destructive distillation*. Then we were chiefly concerned with the production of charcoal, now we have to examine more closely the volatile bodies which are obtained.

Experiment 665.—Introduce a number of small

pieces of wood into the iron retort shown in fig. 138, which has been already used in Experiment 259 for

FIG. 138.
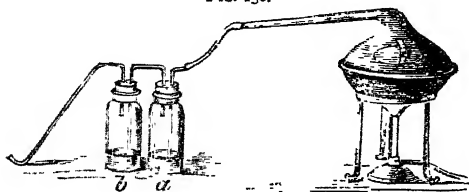
the destructive distillation of coal. The two wash-bottles *a* and *b* should contain a little water only.

When heat is applied to the retort the decomposition which ensues is seen to be accompanied by the evolution of large quantities of gas ; after the expulsion of the air collect in a jar over water some of the gas which issues from the delivery tube and burn it. Note that the gas burns with a highly luminous flame resembling that of coal gas. In parts of the world where wood is abundant and coal scarce this wood gas is used for illuminating purposes. A sample of purified wood gas analysed by Reissig had the following composition in 100 volumes :—

Hydrogen	31·84
Marsh gas (CH_4)	35·30
Carbon monoxide (CO) . . .	25·62
Olefiant gas (C_2H_4) and vapours of	
liquid hydrocarbides . . .	7·24
	100·00

We have, then, evidence in the composition of wood gas that the cellulose—$C_6H_{10}O_5$—breaks up at

high temperatures, and in presence of the natural moisture of the wood, into gaseous bodies some of which contain only one atom of carbon in their molecules—as marsh gas and carbon monoxide—and others two atoms of carbon—as olefiant gas.

On continuing the heat until evolution of gas ceases, the residue left in the retort is good wood charcoal, and the wash-bottles contain a turbid mixture of wood tar and an acid liquid. The latter is separated by filtration through moist paper ; the wood tar, which includes *creasote*, does not pass through the filter, and is separated.

Just neutralise the acid in the filtered liquid by caustic soda ; if the solution were now distilled, a strong-smelling spirituous liquid named *wood naphtha* would be obtained, but the quantity produced from the amount of wood used in the experiment is too small to be worth collecting. Its odour can, however, be noted while the neutralised liquid is boiled in a capsule. If the solution be evaporated to complete dryness, a saline residue is obtained which consists chiefly of sodium acetate—$NaC_2H_3O_2$. When this salt is treated with dilute sulphuric acid, the well-known odour of vinegar is perceived ; this is due to the liberation of the volatile *acetic acid*,

$$NaC_2H_3O_2 + H_2SO_4 = HC_2H_3O_2 + NaHSO_4.$$
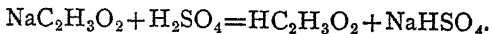
Wood is distilled on the large scale for the purpose of obtaining this acetic acid, or *wood vinegar*. The liquid products are freed from tar, and are neutralised by lime, which forms calcium acetate. On distillation of the solution the acetate is left behind ;

the compound is then heated sufficiently to destroy
tarry matters and distilled with sulphuric acid ; the
condensed product is the crude acetic acid of com-
merce. In the early stage of the distillation of the
solution of calcium acetate a quantity of light
wood naphtha or *Pyroxylic spirit* is obtained ; the
latter when redistilled, so as to separate only the most
volatile portions, gives the purified wood spirit, which
can be easily purchased, and is best suited for experi-
mental purposes. This is a nearly colourless spiri-
tuous liquid, having a peculiar and unpleasant odour
and a burning taste ; it is lighter than water, and
is very freely miscible with it ; it is readily volatile,
and easily combustible, burning with a feebly luminous
flame. This spirit can be used as a source of heat,
and it is largely employed in the arts as a cheap
solvent for various resinous bodies. Good com-
mercial wood spirit rarely contains less than 10 to 15
per cent. of water ; the latter can, however, be almost
wholly removed by the following treatment, which
is very generally employed for the dehydration of
neutral and volatile liquids that are not decomposed
by contact with alkaline substances.

Experiment 666.—Take half a liter of purified
wood spirit, place it in a tall bottle, and add about
100 grams of common pearlash—crude potassium
carbonate—which has been heated to redness in an
earthen crucible, to deprive it of moisture, then
allowed to cool down nearly to the temperature of
the air, and added while still warm to the spirit.
The bottle is well corked, and the mixture shaken at
intervals during two days. The pearlash is a very

hygroscopic substance, and rapidly withdraws water from the spirit, forming either a heavy liquid or a pasty mass, neither of which mixes with the spirit; hence the latter can be poured or drawn off from the heavy solution of the carbonate.

The spirit obtained by this treatment still contains some water which cannot be removed by the pearlash; it is therefore poured into a retort which has been previously filled nearly to the neck with small lumps of fresh quicklime, and is allowed to stand on the lime all night: the dehydrated liquid is then distilled off with the aid of a water-bath. The first 100 cc. should be collected apart and labelled distinctly, as impurities are present in it which will be again referred to; the rest of the liquid which distils over may then be preserved as a specimen of anhydrous and nearly pure *wood spirit.*

Experiment 667.—Place a few drops of the spirit on the deflagrating spoon, fig. 139, and set fire to the liquid; now lower the spoon into a dry jar FIG. 139. of air, allow the combustion to proceed for a short time, then remove the still burning spirit and cover the mouth of the jar with the hand. Note that some moisture has condensed on the sides of the jar, and the residual gas when shaken up with some lime-water causes the usual turbidity indicative of the presence of carbon dioxide. Therefore the wood spirit contains carbon; hydrogen is also present in it, as the moisture produced is water, which results from the combustion of the hydrogen present in the spirit.

When the quantitative composition of pure wood spirit is determined by the methods of *Organic Analysis,*[1] its empirical formula is found to be CH_4O, and molecular weight 32, as deduced from the *vapour density*[2] of the compound.

It has been already pointed out under Experiment 255, that the study of the action of chlorine on marsh gas—CH_4—has led to the conclusion that the latter is a saturated compound, and therefore that carbon is tetratomic. But the above empirical formula of pure wood spirit seems to invalidate both conclusions, as it represents the compound to be an oxide of marsh gas. The evidence already obtained on the other side is so strong, however, that we must seek to explain the constitution of wood spirit in a manner which shall be consistent with the tetratomicity of carbon. The hypothesis that wood spirit is a hydroxyl derivative of marsh gas is perfectly consistent with that view. The meaning of that statement will be rendered clear by the comparison of the following expressions :—

$$\text{Marsh gas, } H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \; ; \text{ wood spirit, } H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH.$$
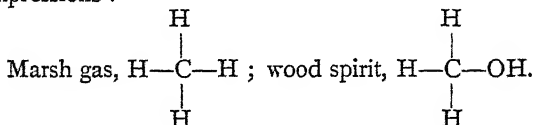
Wood spirit is represented as a compound derived from marsh gas by the *substitution* of one atom of hydrogen by the monad group OH' or hydroxyl.

[1] See Appendix on Ultimate Analysis.

[2] See Appendix on determination of Vapour Density and Molecular Weight.

The soundness of this hypothesis must now be subjected to the test of experiment, and the question arises whether we have the means of recognising the presence of the hydroxyl group in a compound. Reference to Experiment 170 will show that triiodide of phosphorus is capable of acting as a test for hydroxyl, for the action of the iodide on water may obviously be regarded in the following way :—

$$PI_3 + 3HOH = 3HI + P(OH)'_3.$$
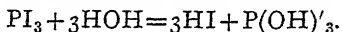
Experiment 668.—Arrange the apparatus represented in fig. 140. The flask should be capable of

FIG. 140.
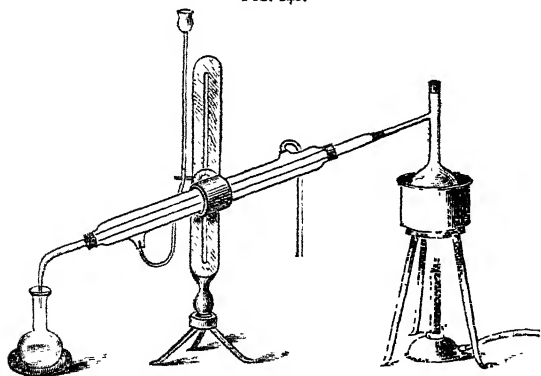
containing about 150 cc., and is preferably of the form shown, with a side tube from the neck, known as an Erlenmeyer flask. Introduce into it one gram of amorphous phosphorus and add 13 grams of iodine in powder. Gently warm the contents of the flask, so as to determine the union of the elements,

and then, when cool, pour in 10 c. cs. of the dehydrated
wood spirit, connect the flask with the condenser,
apply heat to the water-bath, and distil. When
nearly all the liquid has passed over, pour the con-
densed product back into the flask, and distil again,
so as to secure the completion of the reaction.

The distillate is now to be diluted with four or
five volumes of water, when it immediately becomes
turbid, and on standing deposits a heavy liquid
which is slightly coloured by a little free iodine. Add
a few drops of caustic soda solution, and shake the
mixture ; the heavy liquid now subsides as a colour-
less layer, which can be readily separated from its
supernatant liquid by suction into a pipette, whose
dip-tube has been drawn out to a fine point.

The liquid so obtained has an agreeable ethereal
odour ; its specific gravity is 2·23 (water = 1). It is
very volatile, boiling at 44° C. It is almost insoluble
in water. When perfectly pure the composition of this
liquid is represented by the formula CH_3I.

It is evident, then, that wood spirit has ex-
changed hydroxyl for iodine, thus—

$$PI_3 + 3CH_3OH = 3CH_3I + P(OH)_3.$$
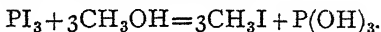
Phosphorus bromide, when made to react with
wood spirit, affords the compound CH_3Br, which is
gaseous at ordinary temperatures, but is liquefied
when cooled below 13° C., which is the boiling-point
of the liquid.

The corresponding chlorine derivative, CH_3Cl,
can be similarly obtained as a colourless gas, which is
only liquefied at −22°. This is easily and simply

produced by the action of hydrochloric acid gas on wood spirit ; when the liquid is heated, much CH_3Cl is evolved, which can be washed by passing through dilute caustic soda, and may then be collected over water ; it can be dissolved in spirit of wine, which absorbs more than 30 volumes of the gas.

The reaction which leads to the formation of this body is represented by the equation,

$$CH_3OH + HCl = CH_3Cl + H_2O,$$
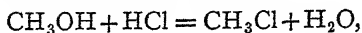
and is obviously analogous to that which takes place when hydrochloric acid acts on potassium hydrate,

$$KOH + HCl = KCl + H_2O.$$
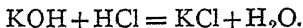
Having ascertained that the group OH can be replaced in wood spirit by any of the halogens, it remains to be seen whether the latter can be replaced in turn by hydrogen, and marsh gas result from this final substitution. For this purpose we shall perform

Experiment 669.—Take a flask of 150 c. cs. capacity, fitted with a cork and gas delivery tube, and fill the bulb with granulated zinc; cover the metal with some very dilute sulphuric acid (1 to 20 of water) in order to dissolve any oxide off the surface, which is generally accomplished in a few minutes, and pour off the liquid. Now wash with distilled water twice, and then cover the metal with a solution of copper sulphate containing one part of the salt in fifty of water. Metallic copper is immediately reduced by the zinc, and the latter becomes coated with a reddish-brown deposit, while the solution soon loses

its blue colour; when the liquid is no longer blue, pour it off and replace by a fresh quantity of the copper solution, and when this is decolorised pour off and wash carefully with pure water, and finally with a little spirit of wine. The object of this treatment is to produce what Messrs. Gladstone and Tribe term a 'copper-zinc couple,' which they find to act much more energetically as a reducing agent than zinc alone.

Having prepared the material wherewith to reduce the iodine compound obtained in the former experiment, the latter is now to be mixed with an equal volume of spirit of wine and poured on the metal in the flask. Distribute the liquid as much as possible over the surface of the copper-zinc, insert the cork with its gas delivery tube, and let the latter dip under the surface of water in a pneumatic trough, then immerse the flask in warm water contained in the bath used in Experiment 668. Gas is soon evolved, and a rather slow but steady current is easily maintained by regulating the temperature. 2 c. cs. of the liquid iodide can afford about 700 c. cs. of gas, and the latter is found to possess all the characters of *marsh gas* described under Experiment 254. When allowed to stand over water for some time, to condense the vapour of the iodide and spirit which accompany it, marsh gas in a very pure condition is obtained by this simple and elegant method. The following equation explains the change which occurs in presence of water, as the copper does not seem to undergo any alteration in the process:—

$$CH_3I + Zn + H_2O = Zn{<}^I_{OH} + CH_4.$$
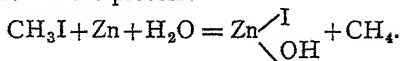
This mode of forming marsh gas is consistent with the view that it is a hydride of the monad group CH_3'; we may therefore place it at the head of the following list of compounds which we have now recognised:—

$$CH_3' \; H' \quad . \quad . \quad \text{Hydride.}$$
$$CH_3' \; I' \quad . \quad . \quad \text{Iodide.}$$
$$CH_3' \; Br' \quad . \quad . \quad \text{Bromide.}$$
$$CH_3' \; Cl' \quad . \quad . \quad \text{Chloride.}$$
$$CH_3' \; OH' . \quad . \quad \text{Hydrate.}$$

The group CH_3' persists in all these compounds and is a monad positive radical termed *methyl*; thus marsh gas is methyl *hydride*, and wood spirit, methyl *hydrate* or methyl *alcohol*. The term 'alcohol' is applied to all similar hydrates of hydrocarbide residues, and the latter, like CH_3, are called 'alcohol radicals.'

The general result of our inquiry so far is that our hypothesis as to the constitution of pure wood spirit has been verified, and we have further learned that this spirit, or, as we shall now call it, methyl alcohol, resembles an ordinary metallic hydrate in the fact that its hydroxyl can be replaced by halogens.

When perfectly pure, *methyl alcohol* is a colourless liquid of peculiar odour. Its specific gravity, when anhydrous, is 0·8136 at 15·5° C. Its boiling point is 58·6° C. (Dupré). It burns in air with a pale blue flame and affords carbon dioxide and water.

Methyl alcohol is a good solvent for iodine, bromine, and many oils and resins. It dissolves anhydrous calcium chloride in large quantity and with the evolution of much heat; when the solution cools, crystals

separate which consist of the compound $CaCl_2,4CH_4O$.
This compound is easily decomposed by water into
calcium chloride and methyl alcohol. Sir Robert
Kane founded on these facts the following process for
the preparation of pure methyl alcohol from crude
wood spirit. The dehydrated spirit is saturated with
anhydrous calcium chloride and the solution distilled
to remove all volatile bodies except methyl alcohol;
water is then added to the contents of the retort to
break up the compound, and the pure methyl alcohol
is then distilled. The product is finally dehydrated
as described under Experiment 666.

The *Synthesis of Methyl Alcohol* from purely in-
organic materials can be effected in the following stages.

1. Marsh gas is formed by passing a current of
sulphuretted hydrogen, charged with the vapour of
carbon disulphide, over metallic copper heated in a
tube. In this case,

$$2H_2S + CS_2 + 8Cu = CH_4 + 4Cu_2S.$$
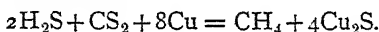
2. Equal volumes of marsh gas and chlorine ex-
posed to diffused light afford, amongst other products,
CH_3Cl (Exp. 255),

$$CH_4 + 2Cl = CH_3Cl + HCl.$$
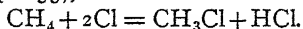
3. Methyl chloride so obtained when heated for
a week to 100° C. in a closed flask with solution of
potassium hydrate is slowly absorbed and methyl
alcohol is obtained,

$$CH_3Cl + KOH = CH_3OH + KCl.$$

Therefore by a comparatively simple series of
operations the first of the alcohols can be built up.

CHAPTER XLVII.

EXPERIMENTS WITH STARCH—CONVERSION INTO A
VARIETY OF SUGAR—FERMENTATION—DISTILLING,
BREWING, &C.—ABSOLUTE ETHYL ALCOHOL.

HAVING gained some knowledge of the nature of the
spirit obtained by the destructive distillation of wood,
we shall now examine the isomer of cellulose, viz.,
starch, in order to ascertain whether it can afford
similar products to those obtained from wood.

Starch is most abundant in the cereal grains—
barley, wheat, and oats—and in various tubers, of
which the common potato is the most familiar
example. When any of these are bruised or broken
up and then washed by a slow stream of water, the
starch particles are separated and soon deposit at
the bottom of any vessel in which the process is con-
ducted as a glistening white granular mass, while the
lighter fragments of husks or cellular tissue float
away in the current. The starch is collected and
dried. When examined under a microscope, it pre-
sents the appearance shown in fig. 142. The
granules vary in size with their source—those of the
potato being large, while the cells of cereal starches
are much smaller. Starch when strongly heated in
partially closed vessels affords products like to those

IV.   C

obtained from wood under similar conditions; but
starch differs from wood tissue in being soluble in

FIG. 142.
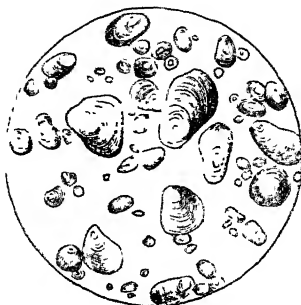
hot water, although insoluble in the cold : hence we
can examine its solution.

Experiment 670.—Stir some starch up with cold
water in an evaporating dish until a thin cream is
formed, then add twice the volume of boiling water
and mix.   Note that the starch swells up and forms a
paste which becomes quite liquid when the contents
of the dish are heated.   If sufficient water be present,
almost complete solution appears to take place.
When this process is watched under the microscope,
the starch granules are seen to swell until the external
membrane is completely distended; the latter then
bursts, and the contents of the little sacs escape into
the water and in great part dissolve in it.   The mem-
branous sacs themselves do not dissolve, but remain
suspended in the liquid.

Add to the dissolved starch a drop of a very

dilute iodine solution, and note the beautiful blue colour developed. We have already employed starch as a test for free iodine (see Experiment 164), and found that the colour is destroyed by heat, but re-appears in cooling the mixture. We have now used the iodine as a test—and the best test—for soluble starch.

Starch undergoes some very important changes when its solution is heated for some time, either with a small quantity of mineral acid, or with the aqueous extract from *partially germinated grain.*

Experiment 671.—Prepare about 300 c. cs. of a starch solution as above described, and add two cubic centimeters of sulphuric acid previously diluted with five volumes of water. Introduce the mixture into a flask of about 1 liter capacity, heat the contents nearly to boiling, and maintain the temperature for some time. Withdraw a few drops at intervals by means of a pipette, and test with iodine. Note that the colour produced changes as the heating proceeds, until the liquid no longer causes a blue tint with iodine, and only affords a reddish-brown coloration. If at this point a few drops are allowed to fall into some strong spirit of wine contained in a test-tube, flocculent matter separates, which is also isomeric with starch, but is distinguished by the above action with iodine, and by rotating a ray of polarised light made to pass through its solution strongly to the *right*; hence the name *dextrine* given to this body.

Now boil the solution for ten minutes and allow it to cool. After this treatment the liquid gives still

less colour with iodine, since by continued boiling in presence of acid the dextrine gradually unites with the elements of water, and is wholly converted into a variety of *sugar* termed *glucose*.[1] When this conversion is complete, the solution is no longer coloured by iodine, but a few drops when warmed with alkaline copper tartrate solution[2] cause a precipitate of cuprous oxide Cu_2O (compare Experiment 480), as glucose (and certain other sugars) are distinguished from starch and dextrine by this reducing action on cupric salts. The ultimate change of starch to sugar is represented by the equation

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6.$$
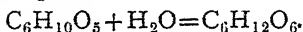
Experiment 672.—Neutralise the free acid in the glucose solution produced in the last experiment by the careful addition of sodium hydrate, and then add to the contents of the flask a small quantity of brewer's *yeast*, or 'barm.'[3] Fit a cork carrying a gas delivery tube to the flask, and let the tube dip under the water in a shallow pneumatic trough, as shown in fig. 143. Invert a jar full of water over the end of the tube to collect any gas evolved, and let the whole stand in a warm place so that the contents of the flask may be maintained at a temperature of about 25° C. (= 77° F.).

After some time the process of *fermentation* com-

---

[1] γλυκύς, sweet.

[2] Prepared by adding tartaric acid to copper sulphate solution, and rendering strongly alkaline by caustic soda. A clear blue solution is obtained if sufficient tartaric acid be added.

[3] If not obtainable from a brewery or distillery, bakers can generally supply it.

mences, the mixture develops a frothy 'head,' and much gas is evolved. The latter is collected after the expulsion of the air previously in the flask, and it

FIG. 143.
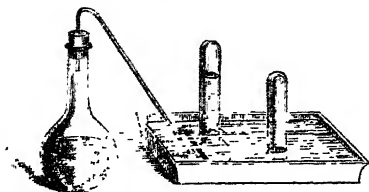
is found to consist chiefly of carbon dioxide, as it does not support the combustion of a taper, and renders lime-water turbid.

The evolution of gas ceases after some hours, and fermentation is at an end. Now observe that the contents of the flask are rather more turbid than they were at first; in other words, the quantity of yeast has *increased* during the process of fermentation. Next open the flask and pour out some of the contents into a test-tube and heat to boiling; note that a disagreeable but distinctly spirituous smell is developed, which is chiefly due to the vapour of a volatile *alcohol*, whose composition is represented by the empirical formula C_2H_6O.

It is easily seen that this alcohol and carbon dioxide can result from the resolution of the glucose [1]—

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2.$$
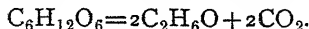
[1] A process for the estimation of glucose in a solution is founded on this reaction; for it has been proved, by direct ex-

By means similar to those adopted in the case of the wood spirit or methyl alcohol, it can be shown that the spirit obtained in the fermentation of starch also contains the hydroxyl group united to the alcohol radical C_2H_5, termed *ethyl*. The two alcohols are therefore closely related—

Methyl alcohol . . . $CH_3'OH$
Ethyl   ,,   . . . $C_2H_5'OH$

Thus, while wood affords the lowest term in the series of alcohols when subjected to a high temperature, the isomer of cellulose—starch—affords the next term by resolution at low temperature under special conditions.

We shall examine ethylic alcohol and many of its derivatives later on, but we are now more immediately concerned with the agent—yeast—which determines the remarkable resolution of the starch-derived sugar into ethyl alcohol and carbon dioxide gas. What, then, is the nature of this body which possesses such exceptional power?

FIG. 144.
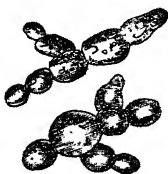
When yeast is examined under the microscope it is seen to consist of numerous minute plant cells. Of these the *saccharomyces cerevisiæ* are shown in process of development in fig. 144. The yeast increases rapidly in a solution of glucose by the growth and division of the cells ; this yeast feeds on a small portion of

periment, that one gram of pure glucose can afford 249 c. cs. of CO_2 gas, measured at 0°C. and 760 mm.

the sugar, while the rest of the latter breaks up chiefly into ethylic alcohol and carbon dioxide. The precise means by which the growing plant accomplishes this resolution is at present a mystery.

Experiment 673.—Connect the flask which contains the fermented liquid obtained in the last experiment with a condenser, or pour the liquid into a retort and rapidly distil over about one-third the total volume of liquid. This has an unpleasant smell, but it contains the alcohol formed during the process of fermentation. In order to detect the latter, add three or four drops of solution of potassium bichromate to about 20 c. cs. of the liquid, then a few drops of sulphuric acid, and heat. The liquid becomes distinctly *green*, while a somewhat *fruity odour* is produced. The reduction of the chromic acid, as evidenced by the change of colour, and the odour developed, serve for the recognition of the alcohol present ; the explanation of this test will be found under Experiment 703.

The dilute spirit obtained in the foregoing operations owes its unpleasant smell to the presence of a small proportion of a liquid termed 'fusel oil.' This is a mixture of bodies, formed during fermentation, whose constituents are chiefly alcohols which boil at higher temperatures than the ethyl alcohol. Advantage is taken of this difference in volatility to purify the spirit on the large scale, but it would be useless to attempt this purification of the small quantity of dilute spirit produced in our fermentation experiment. Nevertheless it is important to learn at this stage how liquids of different boiling points may be separated

and purified by a process termed *fractional distillation*, which is of great value in organic chemistry : hence we make—

Experiment 674.— Mix 150 c. cs. of 'spirit of wine' which boils near 80° C. with 50 c. cs. of 'fusel oil' or amyl alcohol, which is an easily obtained article of commerce, and boils at about 130° C. This mixture represents a strong and highly impure distilled spirit.   Pour the mixture into a flask of 400 or 500 c. cs. capacity, with a side tube, and connected with the usual condensing arrangement as shown in fig. 145.   Introduce a few scraps of old platinum foil into the spirit, as this prevents violent 'bumping' of boiling liquids. Then insert the cork, through which a thermometer, graduated on the stem, should pass. One graduated in half degrees Centigrade is sufficient for ordinary purposes.   The bulb should not project within the body of the flask.

Now apply a rather small Bunsen flame and raise the temperature to the boiling point ; when the latter is reached, so regulate the flame that steady and continuous, but not violent, ebullition shall be maintained.   Such a mixture as that recommended generally begins to boil below 80°, but almost immediately the temperature rises to 84°, and 50 c. cs. can be distilled over at that temperature.   Collect this apart and mark it 'No. 1 fraction.' Continue the steady ebullition, and collect another 50 c. cs. and mark 'No. 2 fraction'; this generally distils over between 85° and 86°. 'No. 3 fraction' of 50 c. cs. is obtained between 86° and 92°, but the mercury then rises rather rapidly until 130° is reached, and

about 20 c. cs. distil during this time : mark the latter
' No. 4 fraction.' The process may then be stopped,
as the liquid left in the flask is nearly pure amylic
alcohol.

Fig. 145.
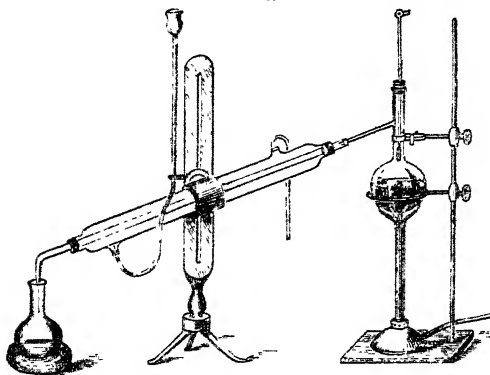
All the fractions have the characteristic odour of
the fusel oil, proving that some is carried over along
with even the first portions of distilled spirit. Now
put 5 c. cs. of each fraction in separate test tubes, and
add 25 c. cs. of water to each, and mix thoroughly.

No. 1 does not become turbid, and no oily drops
can be detected through the liquid.

No. 2 becomes slightly opalescent, and a few
minute droplets can be seen at the surface after stand-
ing for some time.

No. 3 becomes more distinctly turbid and throws
up a few more oily drops than No. 2.

No. 4 scarcely mixes with the water at all, and

therefore chiefly consists of fusel oil, which separates
as a light insoluble layer when added to water.

Thus, owing to the slight miscibility of amyl alcohol
with water, we are able to directly trace the extent of
the separation obtained by this process of fractional
distillation, and we learn that the first fraction contains
the most volatile body in a nearly pure condition,
while the last almost wholly consists of the least
volatile liquid.   It is evident that if the first fraction
be again distilled, it can be further separated into por-
tions, the first of which would contain still less amyl
alcohol, and so on the process can be continued until
pure products are obtained.   When the difference in
boiling point between the constituents of a mixture of
liquids does not exceed 10 degrees, the difficulty of
separating them is much increased, and a larger
number of redistillations are necessary, while, in some
instances, liquids cannot be separated by this method
at all.

The number of distillations required in any given
case may be considerably reduced by the use of the
tube represented, fig. 146, which has been devised
by Glynsky, and is the most effective of the many
forms of apparatus devised to facilitate purification of
mixed liquids by fractional distillation.   The tube f
passes through the cork of any ordinary flask ; the
thermometer is inserted at t, and its bulb is pushed
down a little below the point at which the side tube
a is joined.   The latter carries the vapour to the con-
denser.   The separation of liquids of different boiling
points takes place in the bulbs, three of which are
provided with little glass balls to act as valves.   The

vapours arising from a boiling liquid lift the balls
and escape upwards, but the less volatile quickly con-
dense on the sides of the bulbs
and fall back; they are, however,
prevented from returning to the
flask by the balls ; fresh vapour
has to bubble through successive
layers of liquid so condensed,
and the separation of bodies of
higher boiling point is thereby
facilitated, while any more vola-
tile liquid that may have con-
densed in the bulbs at first is
again vaporised. Thus the steam
undergoes successive 'washings'
in the bulb apparatus, and the
liquid condensed at a given tem-
perature is found to be in a state
of much greater purity than it can
be obtained at a single operation by the simple flask
arrangement. When much liquid has condensed in
the bulbs, it bubbles up into *b* and then overflows
into the by-way *c*, which conducts it back into the
flask. There is always a column of liquid in the U
bend of *c* which prevents the vapour passing in that
direction rather than through the bulbs.
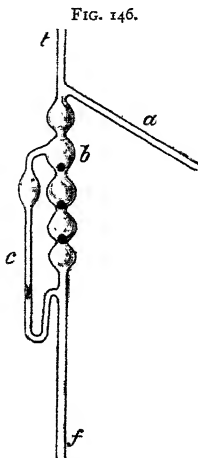
The Manufacture of Spirits on the large scale in-
volves the three operations completely illustrated by
the experiments already made, viz. 1st, *Conversion of
starch into sugar* ; 2nd, *Fermentation* ; 3rd, *Distilla-
tion.*

1st. The starch is usually obtained from barley

which contains about 55 per cent. of starch.   The
grain is moistened and then maintained at a tempe-
rature of about 25° C., when it begins to grow and
throws out a minute sprout.   During germination a
small quantity of a soluble nitrogenous body is formed,
called *diastase*, which possesses the remarkable power
of changing about 2,000 times its weight of starch
into soluble dextrine and ultimately into a ferment-
able sugar ; such a change is effected to a small extent
even in the seed.   When growth has proceeded suffi-
ciently, it is stopped by heating the grain on a kiln or
species of oven.   By this treatment the germinated
barley is converted into *malt.*   This malt is then
bruised and 'mashed,' which latter operation consists
in extraction with water at a temperature of about
70° C.   The solvent action of the diastase is now
fully exerted, the starch dissolves and is gradually
changed into dextrine and ultimately into glucose.[1]
The diastase is able to render more starch soluble
than is to be found in the malt from which it is
derived : consequently unmalted barley, oats, &c., are
often added.   When the extraction is complete, the
mixture is boiled and then strained off.

2nd. The liquor obtained in the last operation
flows into the *fermenting* vats, where it is mixed with
yeast and allowed to 'work' until the starch products
have been converted into alcohol.

3rd. The fermented liquor is pumped into great
stills fitted with trains of condensing apparatus which
act in a similar way to the bulbs in Glynsky's tube ;

---

[1] The term *Maltose* is applied to this form of sugar, which is
the product of the action of diastase and water on starch.

that is to say, the vapours are subjected to successive condensations, whereby the less volatile bodies which constitute the foul-smelling ' feints ' or ' fusel oil ' are gradually separated and drawn off, while the nearly pure and strong spirit is collected apart. The strongest *Rectified Spirits* thus obtained by a process of fractional distillation on the large scale rarely contains less than 15 per cent. of water, which latter can only be removed by the chemical method employed in Experiment 666.

In the process of *Brewing* the malt is mashed as already described, but much greater care is taken in the selection of the malted grain, and hops are added during the process of extraction ; the liquor is then carefully fermented. But the brewer (unlike the distiller, who aims at the production of the maximum quantity of spirit) does not allow the process to proceed beyond the point at which 5 or 6 per cent. of spirit is formed from the glucose, as he desires to leave much dextrine unchanged in order to give ' body ' to the finished product. Consequently when sufficiently fermented the liquor is racked off into settling tanks, where the head of yeast is thrown up and cleared off, while some subsides to the bottom of the liquid, but enough remains to continue a slight fermentative action when the liquor is stored in casks or bottles. In the case of *Ale* only pale malt is used, *i.e.* that which has not been dried at a high temperature. The dark colour of *Porter* or *Stout* is due to the use of a certain proportion of malt which has been heated to such a temperature as to almost char it and

resolve much of the starch into soluble coloured products resembling those from ‘burnt sugar.’

The ethyl alcohol present in the various *Wines* is derived from the grape sugar or glucose present in the juice of the ripe fruit ; a body analogous to yeast is derived from the skins, and this sets up fermentation when the grape juice is exposed to a temperature favourable to the rapid development of the ferment. The colour of red wines is extracted from the dark grape skins during the fermentation.

The spirit distilled from wine is termed *Brandy*, which is alone, strictly speaking, ‘ spirit of wine.’ *Rum* is the spirit distilled from fermented molasses—the mother-liquor from which cane sugar has crystallised.

Experiment 675. — Dehydrate some rectified spirits by the successive action of potassium carbonate and lime, as in Experiment 666 ; *absolute alcohol* is obtained. This is the body whose composition is represented by the formula C_2H_5OH. Note that it is a colourless, very mobile liquid, which has a strong and characteristic odour and a burning taste. It boils at 78·3° at mean pressure. Its specific gravity at 15·5° is ·7935 (water = 1·0) according to the most recent determination. Alcohol burns with a non-luminous flame if slightly hydrated, but the flame of perfectly anhydrous alcohol is somewhat luminous.

Alcohol is a good solvent for many resinous and oily bodies, and for large numbers of organic as well as for some inorganic compounds. When perfectly anhydrous, it dissolves BaO [1] and gives a yellowish

[1] An excellent process for this complete dehydration of alcohol consists in allowing the liquid to stand on some anhy-

solution which is quickly rendered turbid by the addition of a little hydrous alcohol, because barium hydrate, $Ba(OH)_2$, is at once formed and precipitated, since it is quite insoluble in the liquid.

Alcohol mixes freely with water, and, in doing so, much heat is developed; when the mixture cools down, its volume is less than that of the original liquids. The maximum contraction occurs when one molecule of alcohol and three of water are mixed.

Rectified spirit contains about 84 per cent. of absolute alcohol, its specific gravity is about ·838. 'Proof spirit' contains 49 per cent. of absolute alcohol; its specific gravity is ·92 at 15·5° C. The term 'proof' had its origin in the old practice of testing spirit with gunpowder; some of the latter was covered with the spirit to be tested, which was then inflamed; if it burned away without igniting the powder, it was 'under proof,' for it contained enough water to wet the powder and prevent its ignition; the proportion of alcohol was more than 49 per cent., the powder went off.

Methylated spirit is rectified spirit containing one-tenth of its volume of crude wood spirit; the latter communicates an exceedingly unpleasant smell which is only removable with great difficulty; hence the Excise permit this mixture to be sold duty free. This concession has proved a great boon to manufacturers, as the spirit, though useless for drinking, is quite as

drous BaO; after the latter has removed all the water, the dry alcohol then dissolves some of the oxide. The solution is distilled.

suitable for almost all other purposes as the pure alcohol.

The following table gives the usual percentages of absolute alcohol present in the undermentioned liquors :—

Whisky .	. about	45	per cent.
Brandy .	,,	40	,,
Rum .	. ,,	40	,,
Port .	from 17 to 20	,,
Madeira.	,, 16 ,, 18	,,
Sherry .	,, 13 ,, 17	,,
Champagne	,, 10 ,, 12	,,
Claret .	,, 7 ,, 11	,,
Hock .	,, 6 ,, 9	,,
Ale and Porter	,, 5 ,, 7	,,
Cider .	,, 4 ,, 5	,,

CHAPTER XLVIII.

EXPERIMENTS WITH ETHYL AND METHYL ALCOHOLS
—RELATED HYDROCARBIDES—PARAFFINS. SALTS
OF ALCOHOL RADICALS—ESTERS. OXIDES OF THE
RADICALS—ETHERS.

HAVING now learned the conditions under which methyl and ethyl alcohols can be derived from wood and starch respectively, and ascertained their general characters, we have next to examine the chemical changes in which they can take part. In doing so, however, it will be convenient to devote chief attention to the reactions in which ethyl alcohol is concerned, since its derivatives and the reactions which lead to their production are of most importance.

It has been already stated that the hydroxyl group in ethyl alcohol can be as readily replaced by iodine as that in the wood spirit, but we must now realise this change, and it is desirable to operate on a rather larger scale than in the former case, since ethyl iodide is an important reagent and it is well to obtain a moderate supply for future use.

Experiment 676.—6 grams of red or amorphous phosphorus and 40 c. cs. of absolute alcohol, or very strong spirit of wine, are introduced into the flask used in Experiment 668. 60 grams of powdered iodine

are added in small quantities at a time, and the mixture is allowed to stand overnight. When distilled from the water-bath until nothing more passes over, and the product is diluted with water, a heavy liquid separates, which is to be washed with dilute caustic soda to remove free iodine, and is then drawn off by a pipette and poured on some dry calcium chloride previously placed in another small distilling flask. Any water present is removed by the chloride, and the pure ethyl iodide—C_2H_5I—can be distilled off at the temperature of the water-bath.

When the proportions above recommended are used, much phosphoric acid is formed, rather than phosphorous acid, according to the equation—

$$5I + 5C_2H_5OH + P = 5C_2H_5I + PO(OH)_3 + H_2O.$$
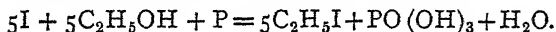
The acid reacts with the excess of alcohol, and some ethyl phosphate remains in the retort.

Ethyl iodide is a colourless liquid when pure, but quickly becomes brownish when exposed to light, owing to the separation of iodine. Its specific gravity is 1·975, and its boiling point is 72·2° C. It is slightly soluble in water, and easily miscible with alcohol, ether and chloroform.

In experimenting with methyl iodide we ascertained that the iodine of the latter can be replaced by hydrogen with the production of methyl hydride or marsh gas. Reasoning by analogy, we should expect ethyl iodide to afford ethyl hydride, a hydrocarbide which should bear the same relation to ethyl alcohol that marsh gas does to wood spirit. We shall test the validity of this reasoning by the next experiment.

Experiment 677.—Arrange the apparatus as in Experiment 669, prepare a fresh copper-zinc couple by Gladstone and Tribe's method already described, and add 3 c. cs. of ethyl iodide previously mixed with an equal volume of alcohol. When the flask is immersed in warm water, evolution of gas commences, and a current is easily maintained as long as there is iodide to be decomposed, if the temperature be maintained between 70° and 80° C. After expulsion of air, a colourless gas can be collected over water, in which it is but slightly soluble, and when tested it burns with a somewhat luminous flame. The composition of this body and its specific gravity accord with the formula C_2H_6. It is therefore the hydrocarbide we expected to obtain from ethyl iodide.

Like marsh gas this hydrocarbide is a saturated compound, for when acted on by chlorine it first affords ethyl chloride, and then successive products by replacement of hydrogen atoms until C_2Cl_6 is obtained.

Dr. Hofmann named this gas *ethane,* and marsh gas *methane,* the terminal *ane* serving to indicate this particular series of saturated hydrocarbides, other members of which will be found in the list on page 37. The following diagram represents the first two hydrocarbides as saturated compounds—

$$\text{Methane, } C \Big\langle \begin{matrix} H \\ H \\ H \\ H \end{matrix} \quad : \quad \text{Ethane, } \Big| \begin{matrix} C \langle \begin{matrix} H \\ H \\ H \end{matrix} \\ C \langle \begin{matrix} H \\ H \\ H. \end{matrix} \end{matrix}$$
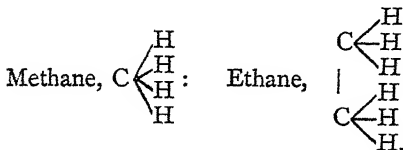
The group of hydrocarbides to which methane and ethane belong is usually named the *paraffin* group, since the fusible solid of which many varieties of candles are now made is a mixture of hydrocarbides of the same series ; and this mixture is named paraffin (*parum affinis*), because it resists the attack of even such powerful chemical agents as sulphuric and chromic acids.

The solid paraffins are found amongst the last products of the distillation of tar, while a number of liquid paraffins distil over in the earlier stages of the process. The mineral or petroleum oil, now so much used for illuminating purposes, consists almost exclusively of a mixture of liquid hydrocarbides of the same group.

The following is a list of the chief normal 'paraffins' and of their related alcohols. The isomers of both series of bodies are very numerous, but they need not be considered at present.

The paraffins from butane to cetane are met with in petroleum or mineral oils, and the remaining two are probably present in the solid 'earth wax' or *ozokerit.*

Of the alcohols those from ethyl to amyl are obtained during fermentation ; hexyl and octyl alcohols indirectly from the oil extracted from the seeds of *Heracleum giganteum* ; heptyl from castor oil ; cetyl alcohol from *spermaceti* ; ceryl alcohol from Chinese wax, and mellisyl (or 'myricyl') alcohol from common beeswax

Hydrocarbides.			*Alcohols.*		
	B.P.			B.P.	
Methane . .	Gas	CH_4	Methyl .	58·6°	CH_3OH
Ethane . .	,,	C_2H_6	Ethyl .	78·4°	C_2H_5OH
Propane . .	,,	C_3H_8	Propyl .	97·4°	C_3H_7OH
Butane . .	1°	C_4H_{10}	Butyl .	117·0°	C_4H_9OH
Pentane . .	38°	C_5H_{12}	Pentyl (Amyl)	} 137·0°	$C_5H_{11}OH$
Hexane . .	70°	C_6H_{14}	Hexyl .	157·0°	$C_6H_{13}OH$
Heptane . .	99°	C_7H_{16}	Heptyl .	175·5°	$C_7H_{15}OH$
Octane . .	124°	C_8H_{18}	Octyl .	196·5°	$C_8H_{17}OH$
Nonane . .	148°	C_9H_{20}	Nonyl .	—	$C_9H_{19}OH$
Solid.			Solid.		
	M.P.			M.P.	
Cetane . . (Palmitane) .	} 278°	$C_{16}H_{34}$	Cetyl .	50°	$C_{16}H_{33}OH$
Cerotane . .	—	$C_{27}H_{56}$	Ceryl .	82°	$C_{27}H_{55}OH$
Mellitane .	—	$C_{30}H_{62}$	Mellisyl .	85°	$C_{30}H_{61}OH$
General formulæ	C_nH_{2n+2}.		. . .	$C_nH_{2n+1}OH$.	

The paraffins differ in composition by CH_2 or its multiples, and form a 'homologous series,' the physical properties of whose members change with tolerable regularity as the molecular weight increases; thus while the lower members are gases at ordinary temperatures, pentane, hexane, &c., are liquids of decreasing volatility, and the higher members are solids.

The alcohols form another homologous series closely related to the first, and amongst them the same gradation in physical properties is observed; on comparing the boiling points of the alcohols, it will be seen that the average difference in boiling point for each increment of CH_2 is about 19·5° C.

We need not pursue this subject further at present,

but shall return to the examination of ethyl alcohol and its derivatives. We shall now prepare some ethyl bromide by a very simple method.

Experiment 678.—Pour 13 c. cs. of strong spirit of wine into a flask of at least 100 c. cs. capacity, then add a previously well cooled mixture of 11 c. cs. of strong sulphuric acid with 6 c. cs. of water, and shake the contents of the flask. When cool add 10 grams of potassium bromide in powder, then connect the flask with a condenser, and distil carefully by means of the gas flame. Ethyl bromide passes over along with some water. There is much frothing at the end, but this does not give trouble if a flask of sufficient size be used. The quantity of bromide obtained almost exactly accords with the equation—

$$H_2SO_4 + KBr + C_2H_5OH =$$
$$C_2H_5 Br + KH SO_4 + H_2O.$$
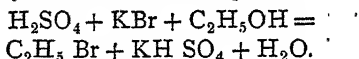
The bromide of ethyl is washed with water, separated and dried by calcium chloride, and redistilled.

As thus obtained it is a colourless liquid of agreeable odour. Its specific gravity is 1·419, and its boiling point 40·7° C. Like the iodide it dissolves very slightly in water, but easily in alcohol and ether.

It is obviously probable that there are two distinct stages in the change which gives rise to ethyl bromide: the first, in which hydrobromic acid is formed by the action of diluted sulphuric acid on the alkaline bromide, and the second stage when the acid reacts with the alcohol thus—

$$HBr + C_2H_5OH = C_2H_5Br + H_2O.$$
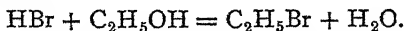
Indeed, ethyl bromide can be formed by the direct

action of hydrobromic acid on ethyl alcohol, but the process is not so satisfactory as that described ; on the other hand, when hydrochloric acid is used instead of hydrobromic acid, *ethyl chloride* is easily produced.

Experiment 679.—Saturate some strong alcohol with hydrochloric acid gas. A large volume is absorbed, and the solution, when subsequently heated in a flask provided with a delivery tube, gives off a gas which, when washed by passing through dilute potash solution, has not any acid reaction, and burns with a greenish flame. This is ethyl chloride formed in the reaction—

$$HCl + C_2H_5OH = C_2H_5Cl + H_2O.$$
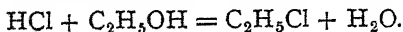
Ethyl chloride is little soluble in water, but is dissolved by alcohol in considerable quantity ; hence the latter is often used to absorb the chloride from mixtures of gases. It affords a colourless liquid if cooled below its boiling point, $11°$ C. When passed into *alcoholic* solution of silver nitrate, the chloride causes a precipitate of silver chloride on warming, while ethyl nitrate is left in solution—

$$C_2H_5Cl + AgNO_3 = AgCl + C_2H_5NO_3.$$
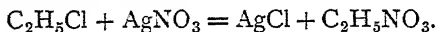
Iodides and bromides of ethyl and of methyl act in a similar way with alcoholic silver nitrate, and double decomposition can also take place when either methyl or ethyl iodide, bromide or chloride, is made to act on insoluble silver salts of various radicals. Thus, if silver cyanide be heated with methyl iodide, it affords methyl cyanide—

$$CH_3I + AgCN = AgI + CH_3CN.[1]$$
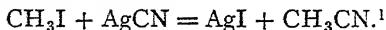
[1] As a matter of fact a mixture of two metameric bodies is obtained—one being the true cyanide of the radical and the

The silver reaction is a general one whereby methyl or ethyl can be made to replace the metal in the metallic salt of any acid. In most cases prolonged digestion is necessary in order to effect complete change, and the following is a usual mode of operating.

Experiment 680.—Take a strong glass tube closed at one end, and about 25 centimeters long and nearly one centimeter in diameter, fig. 147. Before drawing

FIG. 147.
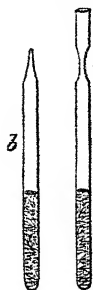
out to a neck as shown at *a*, fig. 147, introduce about one gram of dry silver acetate,[1] then draw the tube before the blowpipe, but in such a way as to leave a stout neck, and pour in about half a cubic centimeter of ethyl iodide. Next gently warm the narrow neck, to remove liquid from it, heat to fusion, and draw off so as to leave a strong end hermetically sealed. The tube should then look like *b*. When cool, mix the contents by shaking, wrap the tube in old cloth secured by cord, and put the whole into warm water contained in any convenient metallic vessel, gradually heat the water to boiling, and after an hour at that temperature allow to cool and uncover the tube. If the latter is strong and has been properly sealed, it will be found uninjured, but the contents will be much altered in appearance, for yellow

other a *carbamine*. The latter is the chief product of this reaction : see chapter LIII.

[1] Easily prepared by precipitating strong solution of sodium acetate with silver nitrate, washing the precipitate with cold water, and drying.

iodide of silver is formed from the white silver acetate, and some liquid is also obtained. On opening the tube by breaking the point, an agreeable fruity odour is perceived : this is due to the presence of ethyl acetate formed in the following reaction—

$$AgC_2H_3O_2 + C_2H_5I = C_2H_5,C_2H_3O_2 + AgI$$
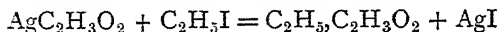
Although this method is one of very general application, it is by no means the most convenient for the preparation of ethyl acetate in quantity, but the following process easily affords it.

Experiment 681.—Introduce into a flask, similar to that used in Experiment 678, 24 grams of dry sodium acetate in powder, and pour upon the salt a cooled mixture obtained by adding 20 c. cs. of strong sulphuric acid very slowly to 20 c. cs. of spirit of wine. After mixing the contents of the flask, distil over about one-third, return this distillate to the flask, and distil again until all liquid has passed over that can be distilled at the temperature of the water-bath.

The reaction in this case is obviously analogous to that which occurred in the production of the bromide :—

$$H_2SO_4 + KC_2H_3O_2 + C_2H_5OH =$$
$$C_2H_5,C_2H_3O_2 + KHSO_4 + H_2O.$$
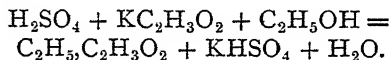
The product is then to be shaken up with some dry potassium carbonate to remove acid and water. On standing, two layers of liquid are formed ; the upper one is light and mobile, and is to be poured off and redistilled.

The product is *ethyl acetate*—the *Æther Aceticus B.P.* It is a colourless liquid of pleasant odour. Its

specific gravity when pure is 0·905, and it boils at 72·7° C. It mixes with about 12 times its volume of water, and in all proportions with alcohol and ether.

Again, *ethyl nitrite*, $C_2H_5NO_2$, can be formed by passing nitrous anhydride gas into alcohol kept carefully cooled, as much heat is evolved during combination ; but the alcoholic solution of the nitrite which is used in medicine—the *Spiritus Ætheris Nitrosi B.P.*—is prepared as follows.

Experiment 682.—Add to 20 c. cs. of spirit contained in a distilling flask 2 c. cs. of strong sulphuric acid, and, when the mixture is cold, add to it, drop by drop,[1] 3 c. cs. of colourless nitric acid. Then introduce 4 grams of fine copper wire, cut in small pieces, and cautiously distil with a thermometer in the neck of the flask. The temperature should not rise beyond 80° C.

The distillate is a fragrant liquid with an apple-like odour. It contains a little *ethyl nitrite*, as well as products of the oxidation of the alcohol. The distillate should measure about 14 c. cs., and when this is diluted with 40 c. cs. of spirit of wine, we obtain the medicinal 'sweet spirits of nitre.'

Pure ethyl nitrite should be obtained by the action of ethyl iodide on silver nitrite ; but as a matter of fact, two metameric compounds are obtained when this method is resorted to, as in the case of the cyanide.

Experiment 683.—Pour 0·5 c. cs. of ethyl iodide on rather more than a gram of pure and dry silver nitrite[2] mixed with some sand in a test tube, and gently

---

[1] With great care, as nitric acid acts very violently on alcohol.

[2] Easily prepared by precipitating strong solution of silver nitrate with sodium nitrite.

warm; action soon begins, and much vapour is evolved while yellow iodide of silver is formed. In this case

$$C_2H_5I + AgNO_2 = C_2H_5NO_2 + AgI.$$
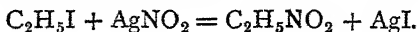
The action is completed by heating the tube with its contents on the water-bath for a short time. During this treatment more vapour is evolved, and this consists chiefly of ethyl nitrite which could be condensed if cooled considerably below the boiling point of the pure nitrite, which is 18° C. The residue of silver iodide is moistened by another liquid boiling at 113°. This is a body termed *nitro-ethane*, which is metameric with ethyl nitrite, but is much more stable than the latter, and does not exhibit any saline structure;[1] in fact it rather acts as a feeble acid and dissolves in caustic potash solution with the production of the compound $C_2H_4KNO_2$. When the contents of the tube are treated by the alkali and the liquid filtered from iodide of silver, the potassium compound is obtained in solution: nitro-ethane—$C_2H_5NO_2$ is, however, easily separated by any dilute acid.

If the constitution of nitrous acid be written as under, the ethyl nitrite and nitro-ethane may be represented thus:—

Nitrous acid	. .	$H-O-N = O.$
Ethyl nitrite	. .	$C_2H_5-O-N = O.$
Nitro-ethane	. .	$C_2H_5-N{<}^O_O$
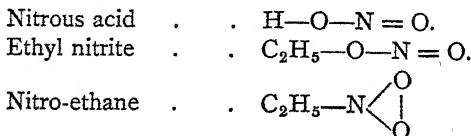
The last body, when acted on by nascent hydrogen, affords the compound $C_2H_5-NH_2$; hence we con-

[1] It is not 'saponified' by caustic potash: see Experiment 686.

clude that in it ethyl and nitrogen are directly united, whereas in the nitrite an oxygen atom is interposed. Further evidence on this point will be obtained later on. Methyl also affords a nitrite and *nitromethane.* Bodies of the latter class are termed *nitro-paraffins.*

Ethyl oxalate can be prepared if 9 grams of neutral potassium oxalate be substituted for the sodium acetate in Experiment 681, but the oxalate and many other analogous salts of ethyl and methyl can be obtained by the direct action of the acid on the alcohol, particularly in presence of *hydrochloric acid.* We shall prepare a little ethyl oxalate by that method.

Experiment 684.—To about 50 c.cs. of spirit of wine add 30 grams of crystallised oxalic acid ; gently warm, so as to dissolve much of the acid, and then pass a current of hydrochloric acid gas into the liquid. The action is assisted by a gentle heat. When the oxalic acid has disappeared the mixture is allowed to stand for some hours, and then poured into water. The ethyl oxalate separates as a heavy colourless liquid. It should be washed with water containing a little sodium carbonate to remove acid, and then distilled from solid calcium chloride.

The *ethyl oxalate* obtained in this way results from the following reaction—

$$2C_2H_5OH + H_2C_2O_4 = (C_2H_5)_2C_2O_4 + 2H_2O.$$
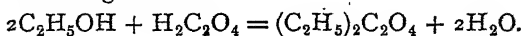
It is a colourless liquid of sp. gr. 1·0824. It boils at 186° C. It is very slightly soluble in water, but is easily miscible with alcohol. By similar processes *methyl oxalate*—$(CH_3)_2C_2O_4$—is readily obtainable from crude wood spirit. It is a crystalline solid, which melts at 51° C. and boils at 162° C.

We already know (Expt. 256) that an excess of sulphuric acid, aided by heat, can tear away the elements of water from alcohol, and produce the hydrocarbide, C_2H_4. When we seek to obtain an ethyl salt of sulphuric acid, we must therefore take care to operate at low temperatures, in order to avoid such a decomposition.

Experiment 685.—Add 50 c.cs. of spirit of wine gradually to an equal volume of strong sulphuric acid, contained in a flask, and keep the mixture at the temperature of boiling water for half an hour ; then set aside to cool. When cold, pour the liquid out into an evaporating dish, dilute with four volumes of water, and add gradually powdered barium carbonate as long as effervescence occurs after fresh additions ; then filter, to remove insoluble barium sulphate, and evaporate the filtrate to a small bulk. Crystals are obtained, which are soluble in rather less than their weight of water, but are not soluble in alcohol. These consist of $Ba''(SO_4C_2H_5)'_2, 2H_2O$.

When a solution of this salt is treated with the exact quantity of sulphuric acid requisite to precipitate all the barium as sulphate, a highly acid liquid is left, which contains hydrogen ethyl sulphate, or *sulphovinic acid*, which can evidently result from the following reaction [1] between alcohol and sulphuric acid—

$$C_2H_5OH + \underset{H}{\overset{H}{\diagdown}}SO_4 = \underset{H}{\overset{C_2H_5}{\diagdown}}SO_4 + H_2O.$$
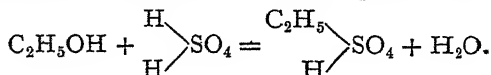
The inverse change readily takes place when sulpho-

[1] For another reaction which can take place between alcohol and sulphuric acid, see Experiment 689.

vinic acid is boiled with much water, as it easily breaks up into alcohol and sulphuric acid.

The potassium and sodium salts of sulphovinic acid are easily obtained by precipitating a solution of the barium salt with potassium or sodium carbonate, filtering off barium carbonate, and evaporating.

The normal ethylic salt of sulphuric acid is obtained with difficulty in a pure condition by the continued action of oil of vitriol on absolute alcohol. It is most easily obtained by the action of ethyl iodide on silver sulphate—

$$2C_2H_5I + Ag_2SO_4 = (C_2H_5)_2SO_4 + 2AgI.$$
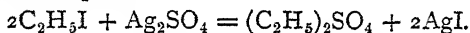
Methyl and other alcohols can afford acids resembling sulphovinic acid, and by similar treatment. These bodies are generally termed *vinic acids.*

The potassium or barium salts of these acids are often used instead of the iodides or bromides of the alcohol radicals in various reactions. For instance, potassium ethyl sulphate added to a strong aqueous solution of potassium sulphydrate affords *ethyl sulphydrate*—

$$C_2H_5KSO_4 + KSH = C_2H_5SH + K_2SO_4.$$
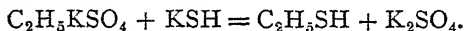
The sulphydrate is obviously the sulphur analogue of alcohol. It is a colourless, offensive-smelling liquid, which boils at 36° C. It readily attacks mercuric oxide, and in consequence is termed *mercaptan* (*mercurium captans*), and affords a white insoluble compound—

$$\begin{matrix} C_2H_5S \\ \\ C_2H_5S \end{matrix}\Big\rangle Hg,$$
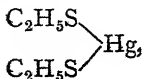
or mercuric mercaptide.

With the exception of the vinic acids and the nitro-paraffins, all the compounds of ethyl and methyl with acid radicals we have hitherto obtained are neutral bodies, which were formed by methods analogous to those that afford ordinary metallic salts. Thus all the evidence justifies the conclusion drawn from the examination of the action of halogen acids on the alcohols, namely, that the latter resemble metallic hydrates in their relations to acids, though they are devoid of alkalinity, and are much more slowly attacked than their mineral analogues.

The ethyl and methyl salts so formed are often termed 'ethers': thus ethyl acetate is 'acetic ether,' ethyl oxalate 'oxalic ether,' and so on. But since another and distinct class of bodies are also termed 'ethers,' we shall follow the German custom, and in future distinguish the salts of alcohol radicals by the general term of *ester*.

The question that next arises is whether an ester can be resolved into alcohol and acid, or a metallic salt of the acid. In other words, can ethyl alcohol and acetic acid be reproduced from ethyl acetate, or the same alcohol and oxalic acid from ethyl oxalate?

In order to obtain an experimental answer to the question we shall make

Experiment 686. — Into a flask of 300 c.cs. capacity pour 5 c.cs. of ethyl acetate, 180 c.cs. of water, and 20 c.cs. of strong solution of sodium hydrate, and mix; a portion of the ester will float for a time. Now fit a cork to the flask, and pass through the cork a straight piece of narrow glass tube fully a meter in length. Secure the flask in an in-

clined position by means of a retort stand, and apply
gentle heat. The long tube serves as a very con-
venient condenser, so that any ethyl acetate vapour
which may distil up is condensed, and returns to the
flask. The ethyl acetate gradually disappears. When
the cooled contents of the flask cease to smell of
ethyl acetate, the long straight tube is replaced by a
short bent piece, whereby the flask can be connected
with an ordinary condenser. On rapidly distilling,
a spirituous liquid is obtained, which gives the
alcohol reaction described under Experiment 673,
while the residue in the flask, when treated with
excess of moderately dilute sulphuric acid, and
heated, affords the characteristic vinegar odour of
acetic acid.

Therefore our question is answered in the affirma-
tive, since prolonged heating of the ester with caustic
alkali has effected its decomposition as follows :—

$$C_2H_5, C_2H_3O_2 + NaOH = C_2H_5OH + NaC_2H_3O_2.$$

| Ethyl acetate. | | Ethyl alcohol. | Sodium acetate. |
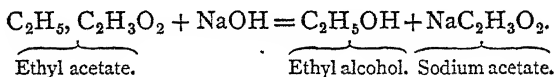
Decomposition of any ester in this way by means
of caustic alkali is termed *saponification*, because of its
analogy with the process of soap-making. A natural
fat is an ester (or mixture of esters) which on heating
with caustic soda is gradually resolved into *soap*—the
sodium salt of an acid analogous to acetic acid—and
an alcohol, *i.e.* common *glycerin*.[1]

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[1] For the particular reactions involved in soap-making, see
GLYCERIN.

Prolonged heating of an ester with much water in a pressure-tube (*see* fig. 147) will gradually resolve the compound into alcohol and free acid. Such a resolution, when brought about by the action of water only, is often termed *hydrolysis*.

The general result, then, is that the esters give evidence of distinct saline structure as well by their decomposition as by their mode of formation from the alcohols.

We shall now seek to trace the analogy between an alcohol and a metallic hydrate in another direction. It is well known that the hydrogen of sodium hydrate can be replaced by an atom of sodium with the formation of disodium oxide—Na_2O. Similarly the hydroxyl hydrogen of ethyl and methyl alcohols should be replaceable by sodium with the production of ethyl and sodium oxide, C_2H_5ONa, or methyl and sodium oxide, CH_3ONa.

Experiment 687.—Pour 5 c.cs. of absolute ethyl alcohol into a test-tube and throw a small pellet of clean sodium into the liquid; the metal dissolves, at first rapidly, with the evolution of much hydrogen gas which can be burned at the mouth of the tube. As successive pieces of the metal are added, solution takes place more slowly, and after a time gentle heat is required to dissolve the last particles of metal. If the liquid be then slowly heated so as to vaporise the excess of alcohol, a white crystalline body separates which consists of $C_2H_5ONa,3C_2H_5OH$. When that body is carefully heated in a current of hydrogen, the

IV.   E

alcohol is driven off, and ethyl sodium oxide, or *sodium ethylate*

$$C_2H_5OH + Na = \underbrace{C_2H_5ONa}_{\text{Sodium ethylate}} + H$$
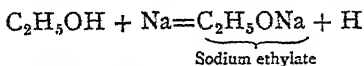
is left as a whitish solid.

The alcoholic solution of sodium ethylate is used as a powerful caustic ; the compound dissolves in water, but is decomposed into alcohol and caustic soda.

Methyl and other alcohols afford analogous sodium oxides. Potassium acts on alcohols like sodium.

If, then, we can replace the hydroxyl hydrogen in alcohol by sodium, &c., it should be possible to replace the hydrogen by *ethyl* and so obtain diethyl oxide, the analogue of disodium oxide ; and the sodium ethylate just produced should afford such a body by its action on ethyl iodide, according to the equation—

$$C_2H_5ONa + C_2H_5I = NaI + (C_2H_5)_2O.$$
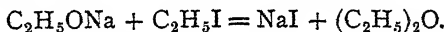
Experiment 688.—Dissolve the sodium ethylate obtained in the last experiment in a little absolute alcohol, and add to the solution a few drops of ethyl iodide. On gently warming, the odour of ethyl oxide (common ' ether ') is distinguishable, if too much iodide has not been employed, while sodium iodide separates from the alcoholic solution. Sodium methylate and methyl iodide similarly react and afford methyl oxide, $(CH_3)_2O$, which is a gas at ordinary temperature.

If, however, *ethyl* iodide be made to act on sodium *methylate*, a ' mixed ether ' is formed, or methyl-ethyl oxide, thus :—

$$CH_3ONa + C_2H_5I = NaI + CH_3OC_2H_5.$$
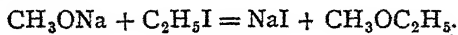
A great number of similar bodies can be obtained by varying the reagents. These are the compounds properly called ' ethers.'

It is obvious that the oxides $(CH_3)_2O$ and $(C_2H_5)_2O$ should also be obtained by the removal of the elements of water from two molecules of the respective alcohols, for, theoretically,

$$2(C_2H_5OH) = (C_2H_5)_2O + H_2O.$$
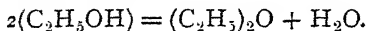
As a matter of fact the *Æther B.P.*, commonly, but incorrectly, called 'sulphuric ether,' is obtained by such a method in which sulphuric acid is the dehydrating agent, though the theory of the action is not so simple as the above equation seems to indicate. We shall now prepare a little ordinary ether by the method usually employed for this purpose. Before the process is described, however, it is well to remind the reader that we have already obtained two widely different products by the action of sulphuric acid on ethyl alcohol. In Experiment 256 olefiant gas (C_2H_4) was produced when the alcohol was quickly heated with a considerable excess of the strong acid ; here *one* molecule of the former lost the elements of water. Again, in Experiment 685, when the alcohol was in excess and but little heat applied, sulphovinic acid, C_2H_5H,SO_4, was formed. Thus the result depended on the conditions of the experiment ; we have now to learn that a further change in the mode of operating enables us to obtain a third product from the same materials.

Experiment 689.—Pour into the distilling flask,

shown in fig. 148, 120 c.cs. of strong spirit of wine, and
cautiously mix with it 100 c.cs. of strong sulphuric
acid. Connect the flask with a good condenser, then
insert a cork *c*, through which passes the narrow glass
tube having a stopcock at *s*; the latter, when connected
by an india-rubber joint with the tube proceeding
from the bottle *b* (which should contain 400 c. cs.
of spirit), serves to control the flow of alcohol into the
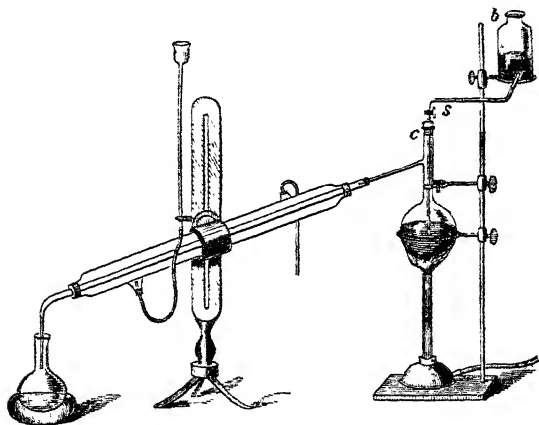
Fig. 148.

flask. At first the stopcock is closed; the contents of
the flask are then heated until they boil freely (at
about 145°C.), and a slow stream of alcohol is then
allowed to flow in from the reservoir by regulating the
stopcock. It is well to immerse the receiver in a
freezing mixture (crystallised sodium sulphate and
common hydrochloric acid), as the principal product

is very volatile and requires efficient condensation. Moreover the ether vapour forms an *explosive mixture* with air ; consequently the operation should not be conducted near a fireplace, nor should a flame be allowed close to the receiver.   The condensed liquid chiefly consists of a mixture of ether and water ; the former separates as a light layer.   Williamson has closely examined this process and shown that the etherification involves the intermediate production of sulphovinic acid, and the latter then reacts with another molecule of alcohol, forming ether, water, and sulphuric acid.   Thus in the first stage—

$$C_2H_5OH + H_2SO_4 = (C_2H_5)HSO_4 + H_2O.$$

In the second stage—

$$(C_2H_5)HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4.$$
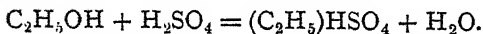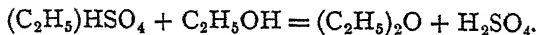
By this 'continuous process' an indefinite amount of alcohol should, theoretically, be converted into ether by a small quantity of sulphuric acid.   In practice, however, it is not desirable to make the acid etherify more than about five times its volume of alcohol, as products of secondary decompositions gradually accumulate in the acid and impede its further action.

The ethereal layer is poured off into a bottle and shaken up with its own volume of water containing a little calcium hydrate to remove acid ; the washed ether is then transferred to a flask containing some lumps of calcium chloride, by which it is dehydrated ; another distillation gives nearly pure ether.

So obtained, *Ether* is a colourless, very mobile

liquid of strong and characteristic odour; its specific gravity is about o·720, and its boiling-point so low (34·5° C.) that the heat of the hand is sufficient to make it enter into violent ebullition.

Its rapid vaporisation in a current of air affords an easy means of obtaining very low temperatures.

Ether dissolves in about nine times its volume of water, with which it slowly unites and reforms alcohol; but it is miscible in all proportions with alcohol and with most oils, while it is an excellent solvent for fats and resins. It is extensively used as an anæsthetic.

Methyl oxide $(CH_3)_2O$ is easily obtained as a colourless gas when methyl alcohol is heated with twice its volume of sulphuric acid.

The analogous *sulphides* of methyl and ethyl are obtained by the action of the corresponding iodides on potassium sulphide dissolved in alcohol—

$$2C_2H_5I + K_2S = (C_2H_5)_2S + 2KI.$$
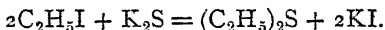
Ethyl sulphide is a colourless liquid of most offensive smell; it does not mix with water. Its specific gravity is o·8367, and its boiling-point 73°C.

CHAPTER XLIX.

IN most of the experiments hitherto made we dealt with bodies in which the alcohol radicals were directly combined with *negative* elements or groups, *e.g.* with iodine in C_2H_5I and CH_3I, with oxygen in $(C_2H_5)_2O$, with hydroxyl in C_2H_5OH and CH_3OH, or with the acidic groups in $C_2H_5NO_2$ and $C_2H_5,C_2H_3O_2$. It is true that we produced the ethylate, or 'alcoholate,' C_2H_5ONa, in Experiment 687, but the result of the reaction of the compound with ethyl iodide indicated that the positive element sodium is only connected with the alcohol radical by means of oxygen. The interesting question then arises whether compounds can be obtained in which a metal and alcohol radical are combined without the intervention of oxygen.

We have already learned, from Experiment 677, that zinc, or Gladstone and Tribe's copper-zinc couple, reduced ethyl iodide to ethane in presence of water or alcohol. If now we act on ethyl iodide with the *dry* copper-zinc couple, we should expect to obtain either

diethyl, a compound of ethyl with zinc, or zinc eth-
iodide ; that is to say, either

$$C_2H_5 \atop C_2H_5 \quad , \quad {C_2H_5 \atop C_2H_5} \!\!\Big\rangle Zn'' \quad \text{or} \quad {C_2H_5 \atop I} \!\!\Big\rangle Zn'' .$$
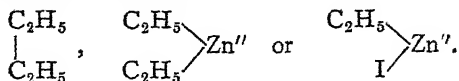
We shall therefore make

Experiment 690.—Place in a flask of the form
shown in fig. 149, and of 50 c.cs. capacity, about nine
grams of fine and clean zinc filings, previously mixed
well with one gram of recently reduced metallic copper
obtained by heating CuO in hydrogen, as in Experi-
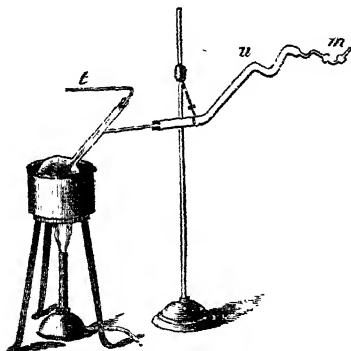
FIG. 149.

ment 52. Then fill the flask with *dry* carbon dioxide
gas delivered from a suitable apparatus through the
tube *t*. Now heat the flask over a Bunsen flame,
shaking the metallic powder continuously until the
filings begin to lose their shape and acquire a slightly
brassy appearance ; then shake it up to prevent melt-

ing, and cool. If the operation has been successful, a number of dark greyish granular masses are obtained. When the dry couple has been properly prepared, pour on the mass 5 c.cs. of ethyl iodide ; the side tube of the flask is then connected with the peculiarly shaped condenser u shown in the figure. This is easily produced from a piece of tubing just wide enough to go over the side tube of the flask and be connected with the latter by india-rubber ; m is a little mercury trap to prevent access of air to the apparatus and yet permit the expansion of the carbon dioxide with which the whole apparatus must now be filled. When all air has been expelled, the supply of carbon dioxide may be stopped. The flask is heated in a water-bath, while the condensing tube is supported in the position shown. The temperature of the water is now rapidly raised. At first ethyl iodide distils, condenses in u, and falls back into the flask ; but when the latter is heated to 90° C. the ethyl iodide no longer distils over. The disappearance of the iodide is due to its combination with zinc in the following way :—

$$C_2H_5I + Zn = \begin{matrix} C_2H_5 \\ \diagup \\ I \end{matrix} \Big\rangle Zn''.$$
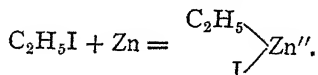
The zinc eth-iodide is formed at 90° C. When this compound is heated to 160° C. it decomposes in the following remarkable manner :—

$$2 \begin{matrix} C_2H_5 \\ \diagdown \\ I \end{matrix} \Big\rangle Zn = \begin{matrix} C_2H_5 \\ \diagdown \\ C_2H_5 \end{matrix} \Big\rangle Zn + ZnI_2.$$
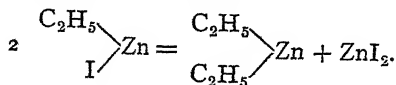
In order to effect this further change, remove the

water-bath and raise the flask until the condenser is
nearly horizontal ; then carefully heat the contents of
the flask by means of a Bunsen flame, while a very
slow current of carbon dioxide passes through the
apparatus. A colourless liquid condenses in the bends
of the tube, and some white smoke issues from the
trap *m*. The liquid is the compound

$$\left.\begin{array}{c} C_2H_5 \\ C_2H_5 \end{array}\right\rangle Zn,$$
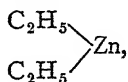
or *zinc ethide.* This is so readily decomposed by
atmospheric oxygen that it undergoes *spontaneous com-
bustion* in air. Hence it must be kept in an atmo-
sphere of carbon dioxide, which gas it does not reduce.
Place a piece of dry white filtering paper on a plate,
rapidly disconnect the flask from the little condenser,
and pour out on the paper the liquid zinc ethide ; if
the temperature be high, the zinc ethide takes fire
in the air and sets up the combustion of the paper
as well. The quantity of zinc ethide formed in the
experiment—little more than three grams—is so small
that the ethide does not always inflame, especially if
poured out on a very cold plate ; but much heat is
always developed, and abundant particles of zinc oxide
are thrown off from the rapidly oxidising body.

This remarkable compound was discovered by
Professor Frankland in 1849, who obtained it by
heating metallic zinc with ethyl iodide in pressure
tubes ; but the Gladstone and Tribe method described
above is much more easily managed and is free from
danger if the directions are exactly adhered to.

Zinc ethide is a colourless liquid of high refractive power. It boils at 118° C. As we have seen, it undergoes complete combustion when exposed to an excess of oxygen; but if the latter be allowed to act upon it very slowly, zinc eth-ethylate is supposed to be first formed—

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \Big> Zn + O = \begin{matrix} C_2H_5O \\ C_2H_5 \end{matrix} \Big> Zn,$$
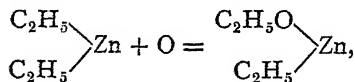
and then zinc ethylate, which can be easily separated—

$$\begin{matrix} C_2H_5O \\ C_2H_5 \end{matrix} \Big> Zn + O = \begin{matrix} C_2H_5O \\ C_2H_5O \end{matrix} \Big> Zn.$$
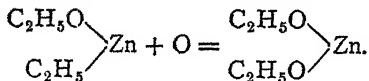
Zinc ethide is soluble without decomposition in pure anhydrous ether.

When the ethide is added to water,[1] energetic action ensues, and pure ethane is produced—

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} \Big> Zn + 2H_2O = \begin{matrix} HO \\ HO \end{matrix} \Big> Zn + 2C_2H_6.$$
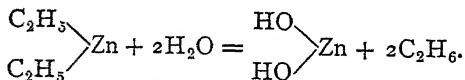
Zinc methide, $\begin{matrix} CH_3 \\ CH_3 \end{matrix} \Big> Zn,$ can be prepared by

similar means from methyl iodide. It is a colourless liquid of very offensive odour. Its boiling point is 46°. It is attacked with great energy by oxygen. On limited oxidation it affords similar products to the

[1] Zinc ethide absorbs ammonia gas and affords ethane and zinc amide $Zn(NH_2)_2$.

ethide. Zinc methide is readily decomposed by water, and affords pure methane—

$$\begin{matrix} CH_3 \\ \diagdown \\ \diagup \\ CH_3 \end{matrix} Zn + 2H_2O = \begin{matrix} HO \\ \diagdown \\ \diagup \\ HO \end{matrix} Zn + 2CH_4.$$
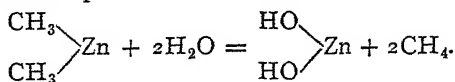
Analogues of zinc methide and ethide can be obtained with other alcohol radicals, and to bodies of this class the general term 'organo-metallic compounds' is applied.   They are reagents of great value, since by their means we can replace chlorine, bromine, &c., in organic molecules by various alcohol radicals ; moreover, they serve for deoxidation and other purposes which will be pointed out in due course. Sodium cannot be substituted for zinc in the preparation of organo-metallic bodies, as ethyl iodide, when heated with the metal, is resolved into sodium iodide and a mixture of ethane and ethylene (C_2H_4) gases ; but when sodium is sealed up in a tube with zinc ethyl, it slowly dissolves and separates zinc. After some time the liquid in the tube deposits fine tabular crystals, which consist of the compound $(C_2H_5)'_2Zn'',C_2H_5'Na'$. Zinc ethide cannot be separated from this body without decomposition of the sodium ethide.

Similar results have been obtained by the action of potassium on zinc ethide.

When *mercury* is sealed up in a tube with ethyl iodide and the mixture is exposed to light, combination slowly takes place, and the crystalline compound

$$\begin{matrix} C_2H_5 \\ \diagdown \\ \diagup \\ I \end{matrix} Hg'',$$ or mercuric ethiodide, is obtained.   By
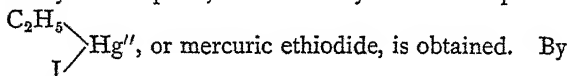
the action of zinc ethide on this compound mercuric

ethide can be obtained as a colourless liquid which is *not* spontaneously inflammable.

$$2 \; \frac{C_2H_5}{I} {>} Hg + \frac{C_2H_5}{C_2H_5} {>} Zn = 2 \; \frac{C_2H_5}{C_2H_5} {>} Hg + ZnI_2.$$
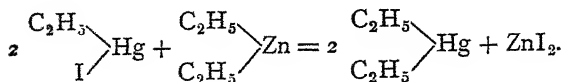
But this is a very troublesome process. Mercuric ethide can, however, be prepared with great facility by a different method, which is in part due to Frankland. This we shall now carry out.

Experiment 691.—Prepare a weak amalgam of sodium in the following way :—Gently warm 400 grams of mercury in a porcelain dish, and throw on the surface some solid paraffin, which soon melts and covers the surface of mercury with a protective layer. Weigh out eight grams of metallic sodium in clean pieces. Stick a small lump of sodium, the size of a pea, on the point of a wire, and plunge the metal rapidly under the surface of the mercury ; combination takes place at once without combustion of the sodium, and successive pieces can be amalgamated in the same way until all the sodium has been added. The contents of the dish are allowed to cool down, when the layer of solidified paraffin can be removed, and the amalgam of sodium can then be poured into a flask. A cork for the latter, provided with a long condensing tube, should be at hand.

Now add to the amalgam ten cubic centimeters of ethyl iodide. No action whatever ensues, even if the contents of the flask are warmed, but the addition of only 2 c.cs. of ethyl acetate suffices to set up brisk action. When the latter has once commenced, it is

liable to become rather too energetic ; hence a vessel
of cold water should be at hand in which the flask
can be plunged from time to time.   The long con-
densing tube prevents loss of ethyl iodide.   When
the action slackens the contents of the flask should be
shaken occasionally, and ultimately the reaction can
be completed by heating in a water-bath.   During
the reaction a white solid separates and at the end
forms a pasty layer on the surface of the mercury.
This white compound is sodium iodide, and the liquid
mixed with it is mercuric ethide resulting from the
reaction—

$$\mathrm{Hg} + 2\mathrm{Na} + 2\mathrm{C_2H_5I} = \begin{matrix} \mathrm{C_2H_5} \\ \diagdown \\ \diagup \\ \mathrm{C_2H_5} \end{matrix}\mathrm{Hg} + 2\mathrm{NaI}.$$
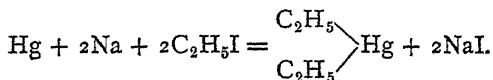
The ethyl acetate used can be distilled off *un-
changed in amount* ; the above reaction does not take
place in its absence, but no satisfactory explanation
has yet been given of the purpose it serves.   When
the acetate has been distilled off [1] at the temperature
of the water-bath, and any unchanged ethyl iodide
with it, water is added to the contents of the flask ;
the iodide of sodium dissolves, and leaves a small
quantity of a colourless heavy liquid, which is the
mercuric ethide, together with the excess of mercury
used in the operation.   Most of the aqueous solution
can be poured off without loss of ethide, and the
latter can then be separated by a pipette.   The ethide

---

[1] This distillate carries with it a little of the mercuric ethide;
when it is mixed with spirit, and alcoholic solution of mercuric
chloride is added, the compound $C_2H_5'Hg''Cl'$ separates.

should be washed with water, in which it is almost insoluble, then with dilute potash, and lastly distilled from some lumps of calcium chloride. Care should be taken not to inhale the vapour, as it is supposed to be poisonous.

Mercuric ethide so obtained is a colourless liquid of peculiar odour. Its specific gravity is 2·44. Some varieties of crown glass have a specific gravity less than 2·4, hence fragments can float in the ethide, whereas flint glass (3·4) sinks. The liquid boils at 159°. It is not dissolved or easily decomposed by water, but is soluble to some extent in alcohol and freely in ether.

Mercuric ethide is not prone to oxidation like the zinc compound, and is therefore a much more manageable reagent. If brought into an atmosphere of chlorine, it inflames.

Mercuric ethide, when sealed up in a tube and exposed for some months to strong sunlight, slowly decomposes into mercury and the paraffin *butane* C_4H_{10}, or diethyl. The latter is a mobile liquid while retained under pressure. Its boiling point is 1° C., therefore it is converted into gas on opening the tube.

When mercuric ethide is sealed up in a tube with a large excess of zinc, the latter displaces mercury when heated to 100° for thirty-six hours.

$$\begin{array}{c}C_2H_5 \\ \diagdown \\ C_2H_5 \diagup \end{array}\!\!Hg + Zn = \begin{array}{c}C_2H_5 \\ \diagdown \\ C_2H_5 \diagup \end{array}\!\!Zn + Hg.$$
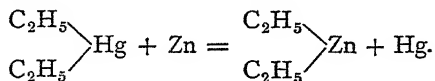
This is the easiest of all methods for the preparation of zinc ethide in moderate quantity.

Mercuric methide, $\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!\Big\rangle Hg$, can be produced by
the action of methyl iodide, mixed with the acetate, on sodium amalgam. The methide is a colourless liquid of specific gravity 3·069. It boils at 94°. By means of zinc ethide or mercuric ethide, other organo-metallic bodies can be obtained, of which the following are the most important :—

Aluminium ethide, $(C_2H_5)'_3Al$. By the action of aluminium on mercuric ethide at 100°, an inflammable liquid is obtained boiling at 194°. The specific gravity of its vapour requires the above formula, and the methyl compound is similar in composition ; hence aluminium acts as a *triad* in combination with alcohol radicals.

Plumbethide, $(C_2H_5)_4Pb$, by the action of zinc ethide on lead chloride. This is a liquid of specific gravity 1·62, which boils at 200°. It is noteworthy that this is a compound in which lead acts as a distinct *tetrad.* The ethide, $(C_2H_5)_6Pb_2$, is also known.

With *tin*, ethyl forms the compounds $(C_2H_5)_2Sn$, $(C_2H_5)_4Sn$, and the intermediate $(C_2H_5)_6Sn_2$.

The non-metallic elements, nitrogen, phosphorus, arsenic, boron, silicon, &c., also combine with ethyl, methyl, and their homologues ; these are compounds which we can more conveniently examine at another stage of our inquiry. See Chapter LIII.

CHAPTER L.

THE next stage of our inquiry obviously involves the
study of the products of oxidation of the alcohols.
We do not now refer to those extreme cases in which
they undergo complete combustion into carbon di-
oxide and water, but rather to such *limited oxidation*
as can take place without the total disruption of the
alcohol molecules.

We have already met with a body among the
products of the destructive distillation of wood which
contains the same number of atoms of carbon as ethyl
alcohol ; that body is *acetic acid.* When we compare
the empirical formulæ of the two compounds—

$$C_2H_6O\text{—Ethyl alcohol,}$$
$$C_2H_4O\text{—Acetic acid,}$$

we see that the acid differs from the alcohol in con-
taining two atoms *less* of hydrogen and one atom *more*
of oxygen. It is therefore conceivable that the acid
could be derived from the alcohol by the action of
two atoms of oxygen on the latter, one oxygen atom
removing hydrogen, with which it should form water,

while the second atom could step into the place of the hydrogen removed. If this view be correct, it is obviously possible that such a change can take place in *two distinct stages*. With this much reasoning on previously ascertained facts to guide us we can proceed to the experimental tests.

Experiment 692.—Place in a watch-glass half a gram or so of platinum black, and moisten the latter with pure ethyl alcohol ; then thrust a small piece of blue litmus paper into the paste and cover the glass with a bell jar slightly tilted by a wedge so as to permit a little air to enter. At first the litmus does not change colour, but after a time it reddens, proving that an acid is produced. If now the bell jar be raised for a moment, a rather agreeable odour will be perceived, more or less resembling that noted in Experiment 673. The cover is replaced, and the oxidation of the alcohol allowed to proceed. At the end of twenty-four hours the paper strip is generally quite red ; if then the watch-glass be gently warmed, a distinct smell of *vinegar*, *i.e.* of acetic acid, will be developed. When the experiment is made on a larger scale, sufficient acetic acid is easily obtained to permit of its complete identification. The platinum black does not suffer any change in this process, and acts merely as a carrier of oxygen.[1] Therefore acetic acid bears the relation to alcohol already suggested, and the final change can be represented by the following equation :

$$C_2H_6O + 2O = C_2H_4O_2 + H_2O.$$

$$\underbrace{}_{\text{Alcohol.}} \qquad \underbrace{}_{\text{Acetic acid.}}$$
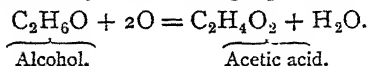
Similar oxidation of alcohol is carried out on a

[1] See Experiment 420.

large scale in the production of *Wine Vinegar.* Casks perforated at the sides with air-holes are filled with wood shavings, generally of beech, and the wood is moistened with vinegar previously mixed with some fermenting grape-juice. A special ferment (*mycoderma aceti*) is developed after a short time, and this acts somewhat like the platinum black in our experiment, for when weak wines are allowed to trickle over the shavings in presence of the air admitted to the cask, oxidation takes place with considerable rapidity, much of the alcohol is converted into acetic acid, and a liquid issues from the bottom of the cask which only requires a repetition of the process and final clarification to afford good wine vinegar.

Pure acetic acid can be obtained either from wine vinegar or wood vinegar by neutralising with caustic soda, as described at page 7, crystallisation of the sodium acetate formed, and decomposition of the salt with sulphuric acid.

Experiment 693.—Heat about 50 grams of crystallised sodium acetate—$NaC_2H_3O_2,3H_2O$—in a porcelain dish until the whole of the water of crystallisation is expelled ; then allow the residue to cool, and break it up into very coarse powder, which latter should be introduced into a small retort connected with a condenser. Pour on the acetate about 30 c.cs. of strong sulphuric acid, and allow the latter to act for some time, then distil over all the acetic acid.

Acetic acid so obtained is a strongly acid liquid having a very pungent odour. It solidifies at 17° C. to a crystalline mass, and is then termed *glacial* acetic acid. Above 17° it is a liquid of specific gravity

1·0553, which boils at 118°. When water is added to
the pure acid, the specific gravity *increases* until one
molecule of water has been added for each molecule
of acid. At this point the specific gravity is 1·0748.
On further addition of water, the specific gravity
regularly diminishes.

Ordinary vinegar seldom contains more than six
per cent. of real acetic acid.

It is evident from the last experiment that an
acetate can be readily recognised by heating with sul-
phuric acid, when the characteristic odour of vinegar
is developed. The two following reactions complete
the identification.

Experiment 694.—Make a rather strong solution
of sodium or other soluble acetate and divide in two
parts: (*a*) To one add silver solution ; a white
crystalline precipitate forms of silver acetate, which,
however, is soluble in much water, and therefore is not
formed in dilute liquids. (*b*) To the second add
Fe_2Cl_6 solution : a dark red colour is produced, owing
to the formation of ferric acetate, $Fe_2(C_2H_3O_2)'_6$.
The red liquid when boiled throws down a brown preci-
pitate of basic ferric acetate, while the odour of acetic
acid is perceived as a portion escapes with the steam.

A very remarkable synthesis of acetic acid can be
effected by heating *methyl* cyanide with caustic potash ;
ammonia gas is evolved, and potassium acetate is
formed. In consequence of this decomposition
methyl cyanide is often termed *acetonitrile*.

$$CH_3-C\!\!\begin{array}{l} N \\ \vdots \end{array}\!\!\begin{array}{l} +H_2O \\ +H\,OK \end{array} = CH_3-C\!\!\begin{array}{l}{}^{O} \\ {}_{OK}\end{array} + NH_3$$
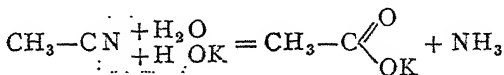
In this reaction we obviously have a mode of passing up from one alcohol radical to a derivative of the next in series. *Ethyl* cyanide, C_2H_5—CN, under similar conditions, affords ammonia and the potassium salt of *propionic acid*, C_2H_5—CO_2H, which bears the same relation to propyl alcohol as acetic acid to ethyl alcohol. Moreover, this mode of formation leads to the conclusion that acetic acid *includes the methyl* (CH_3) *group*, and this is confirmed by the readiness with which sodium acetate affords marsh gas (CH_3H) when heated with caustic alkali (see Experiment 254).

If, then, the above synthesis of acetic acid as well as the decomposition just referred to justify the expression

$$CH_3—COOH,$$
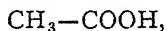
we have to test directly for the hydroxyl group, notwithstanding the fact that on any other view it would be difficult to reconcile the expression —CO_2H with the tetratomicity of carbon.

In this case, as in that of the alcohols, our criterion must be the action of a phosphorus compound with the acid. The trichloride of phosphorus is, however, a more convenient reagent for our present purpose than the tri-iodide before used.

Experiment 695.—Pour into a flask provided with a side tube 10 grams of trichloride of phosphorus. Now insert the cork, having previously passed through it the long stem of the bulb tube shown in fig. 150. Introduce into the bulb of the latter about 15 grams of acetic acid, almost free from water, and therefore capable of solidifying completely when cooled to 10° C. Connect the flask with the condenser, and

slightly open the stopcock so as to allow the acid to drop slowly into the chloride of phosphorus. After

FIG. 150.

addition of the whole quantity of acid, the stopcock is closed, and the contents of the flask are heated by a water-bath. A liquid soon distils over, which fumes in the air ; its vapour has a most irritating effect on the eyes, and also causes violent coughing ; hence the whole operation should be conducted near a chimney with a good draught.
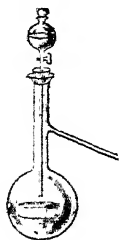
The liquid so obtained is represented by the formula $CH_3-CO-Cl$, and is named *acetyl chloride*, the term *acetyl* being applied to the residue of acetic acid, $CH_3-CO(=C_2H_3O')$. This body evidently results from the reaction [1]—

$$PCl_3 + 3(CH_3-CO_2H) = 3(CH_3-CO-Cl) + P(OH)_3.$$
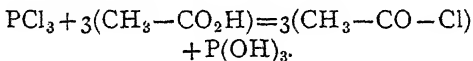
This chloride boils at 55·6° C. The specific gravity of the liquid is 1·1305.

When a few drops are added to water in a test-tube, the chloride falls to the bottom, but shortly energetic action takes place, in the course of which the chloride disappears, and the solution is then easily shown to contain acetic and hydrochloric acids, arising from the reaction—

$$CH_3-CO-Cl + HOH = CH_3-CO-OH + HCl.$$

In the action of phosphorus chloride on acetic acid

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[1] A similar change occurs when sodium acetate is used instead of the acid.

we have evidence that the latter contains *hydroxyl*, while the synthesis of the acid from methyl cyanide supplies evidence of the presence of *methyl* also. The residue is obviously the diad radical CO″, or *carbonyl*, which is directly united to methyl on the one hand and hydroxyl on the other. As we proceed it will be seen that all other organic acids, as well as acetic, contain the group $-COOH$, which is usually termed *carboxyl*.

We have thus arrived at some knowledge of the *structure* of the molecule of acetic acid, and the expression

$$CH_3-CO-OH$$

is the structural or *constitutional* formula of the body, which, it will be observed, is founded on evidence derived from the study of the synthesis as well as of the decomposition of acetic acid. Such formulæ are of great value in chemistry, as they serve to recall the transformations which complex compounds can suffer as well as to suggest new modes of employing them or of effecting their syntheses. The latter, or synthetic, suggestion is useful as a test of the validity of a particular structural formula ; thus, in the case of acetic acid, if the above expression be correct, sodium acetate should result from the action of carbon dioxide on *sodium methide*—

$$CO_2 + \begin{matrix} CH_3 \\ | \\ Na \end{matrix} = CO \begin{matrix} \nearrow CH_3 \\ \searrow ONa \end{matrix}$$
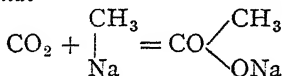
And this reaction has been realised by Wanklyn.

A structural formula which can stand tests of this kind is of importance as a concrete expression for the

changes to which the molecule is subject under usual
experimental conditions.   But the student must care-
fully guard against forming a hard mechanical concep-
tion of the chemical molecule in consequence ; any
definite knowledge we possess tends rather to the con-
clusion that there is constant intramolecular motion
of the atoms, and that their arrangement at any given
moment depends on external conditions.   It is there-
fore quite possible that two or more structural formulæ
can be correctly assigned to a single compound, each
one representing changes determined under different
conditions.   Some instances of this kind will be
noticed as we proceed.

If we add acetyl chloride to excess of anhydrous
sodium acetate, we obtain the *anhydride* of acetic acid.

Experiment 696.—Introduce into a small retort
12 grams of powdered sodium acetate which has been
deprived of water by heat as already described, and
add drop by drop 9 or 10 grams of acetyl chloride.
Cool the retort by partially immersing in cold water.
Allow the mixture to stand for some time, then add a
gram or two more of sodium acetate in very fine powder
and distil.   A liquid passes over which smells like
acetic acid, but, when pure, has not an acid reaction.
Its specific gravity at 15° is 1·079, and it boils at
138° C. The composition of the liquid is $(C_2H_3O)'_2O''$,
and it obviously results from the reaction—

$$C_2H_3OCl + C_2H_3O-ONa = (C_2H_3O)'_2O + NaCl$$
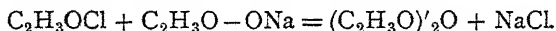
When added to water the oxide remains for some
moments without apparent change, but it dissolves after

a time, and a strongly acid solution is obtained which is found to contain only acetic acid ;[1] the amount of the latter formed from the oxide corresponds with that required by the equation—

$$(C_2H_3O)_2O + H_2O = 2C_2H_3O-OH.$$
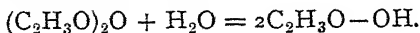
Therefore, acetyl oxide is the *anhydride* of acetic acid.

It is not necessary to prepare the chloride of an acid radical in order to produce the anhydride, as the latter can be directly obtained from the sodium salt of the acid by distillation with oxychloride of phosphorus, thus—

$$4(C_2H_3O-ONa) + POCl_3 = 2[(C_2H_3O)_2O]$$
$$+ NaPO_3 + 3NaCl.$$
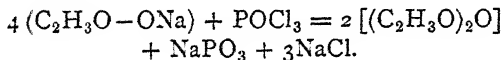
The homologues of acetyl oxide are obtained by similar methods.

Acetyl peroxide $(C_2H_3O)_2O_2$ and its homologues are produced when the anhydride acts on barium peroxide in presence of ether.

When acetic anhydride is added to alcohol, ethyl acetate is formed. Acetyl chloride and alcohol afford ethyl acetate and ethyl chloride. Thus the hydroxyl hydrogen of the alcohol can be directly replaced by *both* these compounds of the acid radicals ; hence the latter can be used as tests for hydrogen so combined.

Acetic anhydride can be reduced to ethyl alcohol

[1] If the oxide contained any unchanged chloride, the aqueous solution of the liquid would give a precipitate with silver nitrate. This is a convenient test for the purity of the oxide.

when treated with sodium amalgam and *snow*, *i.e.*
with nascent hydrogen at low temperature.

$$(C_2H_3O)_2O + 8H = 2C_2H_5OH + H_2O.$$
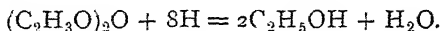
We have already learned from Experiment 695
that but one atom of chlorine can be introduced into
acetic acid by phosphorus trichloride, and then only
in substitution for hydroxyl. We have next to inquire
how far chlorine itself acts on acetic acid.

Experiment 697.—Dissolve about one gram of
iodine in 20 c.cs. of glacial acetic acid, and introduce
into an Erlenmeyer flask connected with a condenser.
Pass a slow current of dried chlorine gas into the
liquid, at first in the cold and then when heated to
100°, and continue to pass the gas until it escapes
without further absorption : this requires several
hours even with a small quantity. Next distil, with a
thermometer in the neck of the flask, and collect all
that passes over above 180° C. This is nearly pure
mono-chloracetic acid $CH_2Cl-COOH$, which boils at
186°, and solidifies below 62° in fine crystalline needles.
By the further action of chlorine *dichloracetic acid*,
$CHCl_2-COOH$, is obtained, which is a liquid even
at 0°, and boils at 191°.

When the chlorine is in large excess and the
mixture freely exposed to sunlight, *trichloracetic acid*,
CCl_3-COOH, is formed. It is a crystalline body
below 52° C ; it boils at 195°. This is the last stage
in the *direct* substitution of chlorine for hydrogen
in acetic acid, for the hydroxyl hydrogen is un-
touched in the operations just referred to.

The only rational explanation of these remarkable

facts is that the hydroxyl hydrogen and that which is directly replaceable by chlorine occupy different positions in the molecule of acetic acid ; while the three atoms successively displaced in the formation of the three chloracetic acids are similarly combined.

The action of chlorine on acetic acid therefore confirms the conclusion already drawn from the synthesis of acetic acid by methyl cyanide (as well as from the ready resolution of the acid in such a way as to afford methyl hydride), namely, that the molecule of acetic acid acts as if it contained the *methyl* group, CH_3, in addition to carboxyl. When the direct relationship already proved to exist between acetic acid and ethyl alcohol is borne in mind, the inference is obvious that the latter also includes the methyl group, and that the two bodies are to be compared as under—

$$CH_3-CH_2-OH-\text{Alcohol.}$$
$$CH_3-CO-OH-\text{Acid.}$$
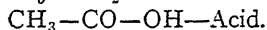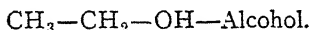
It will be found later on that this view of the structure of alcohol is fully justified by additional evidence. On the other hand the change from alcohol to acid is not so direct and simple as it would appear to be from the above comparison, as an intermediate compound termed *aldehyde* is also formed. But the conditions under which this body is most readily produced will be examined in the next chapter.

We now turn to methyl alcohol, which should afford by oxidation an acid related to it as acetic acid is to ethyl alcohol.

Experiment 698.—Repeat Experiment 692, using methyl alcohol wherewith to moisten the platinum black. As in the former instance, an *acid* is produced which reddens litmus paper ; when the platinum is heated an acid vapour is evolved which is quite distinct in smell from the acetic acid formed when ethyl alcohol is oxidised. The acid consists of CO_2H_2, and is termed *formic acid*, because it was originally met with in the liquid obtained by distilling the bodies of ants (*formicæ*) with water ; the same acid is present in stinging-nettles.

The production of formic acid, even in small quantity, by the oxidation of methyl alcohol is a tedious and troublesome process, but a much more convenient—though irregular—source of the body is oxalic acid, which we have already used in the preparation of carbon monoxide gas.

Experiment 699.—Introduce into a retort about 50 c.cs. of common *glycerine*, and add 30 grams of oxalic acid. Connect the retort with a long-necked flask to act as receiver and condenser, as the bulb can be partially immersed in cold water. On heating the contents of the retort to 100° C. an acid liquid slowly distils over until the whole of the oxalic acid has been decomposed ; the residue left in the retort is glycerine *practically unchanged in amount.* A further addition of 30 grams of oxalic acid can be made and the process repeated.[1] The acid liquid is chiefly an

---

[1] The glycerine will act for an indefinite time. A single quantity of about 75 c.cs. recently served for eleven operations in the author's laboratory without material loss.

aqueous solution of formic acid, resulting from the following decomposition—

$$C_2O_4H_2 = CO_2H_2 + CO_2.$$

$$\underbrace{}_{\text{Oxalic acid.}} \qquad \underbrace{}_{\text{Formic acid.}}$$
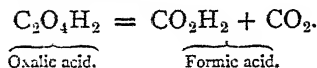
When the acid solution is just neutralised with sodium carbonate, and the liquid is evaporated to complete dryness, sodium formate CO_2HNa is obtained as a neutral salt. If the latter be powdered and mixed with two-thirds of its weight of anhydrous oxalic acid (obtained by heating the crystalline acid to 110° C.) in a retort, the mass becomes pasty, and on the application of gentle heat anhydrous formic acid distils over.

Formic acid is a liquid above 8·5° C.; its specific gravity is 1·22; it boils at 99° C. Like acetic acid it is monobasic, and therefore, following the general rule already stated, it contains one carboxyl group; hence its formula should be written as under, when its relation to acetic acid becomes obvious—

$$H-CO-OH—\text{Formic acid.}$$
$$CH_3-CO-OH—\text{Acetic acid.}$$
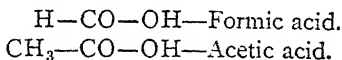
The addition of an atom of oxygen suffices to break formic acid up into carbon dioxide and water; hence (unlike acetic acid) it acts as a powerful reducing agent.

Experiment 700.—Add to solution of mercuric chloride in a test-tube a few drops of formic acid solution and gently warm. A white precipitate slowly appears; this is mercurous chloride, thus formed—

$$2HgCl_2 + H-COOH = Hg_2Cl_2 + CO_2 + 2HCl.$$
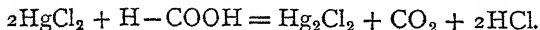
Carbon dioxide gas is evolved. This reaction serves as a convenient *test for formic acid.*

If formic acid be in excess and the liquid be rapidly boiled, the reduction proceeds farther and metallic mercury is obtained.

Ammonia silver nitrate is also reduced by formic acid, as are gold and platinum chlorides.

Phosphorus chlorides break up formic acid into carbon monoxide; consequently neither formyl chloride nor formic anhydride is obtained.

Experiment 701.—Pour some strong sulphuric acid into strong formic acid, or on sodium formate contained in a test-tube, and apply gentle heat. A colourless gas is produced, which can be easily burned at the mouth of the tube. This is carbon monoxide resulting from the removal of the elements of water from the acid—

$$H-COOH = CO + H_2O.$$
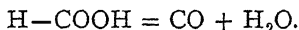
Very pure carbon monoxide gas can be obtained by this method.

The readiness with which formic acid is resolved into carbon monoxide and water suggests a mode of effecting the synthesis of the acid; for if resolution of the latter easily takes place in presence of a powerful dehydrating acid like sulphuric acid, combination should occur between carbon monoxide and water in presence of an alkali.

Experiment 702.—Provide a tube of the form shown in fig. 151. This is easily made by bending a piece of glass tube of 8 or 9 millimeters bore, so as to leave the limb *l* about 50 centimeters in length.

Before drawing out the end s to a narrow tube ready for sealing off, introduce a few fragments of caustic potash about the size of small peas, so that they may rest at the bend b, where they should be moistened by a few drops of water. Now connect s with an apparatus giving a steady current of carbon monoxide, and let the free end of the long limb dip under the surface of the mercury in the jar. When the air has been expelled from the tube, seal at s by a small blowpipe flame, and then support the tube, as shown, over the mercury. Heat is applied at the bend where the potash lies, and the temperature

FIG. 151.

is easily maintained at about 150° C. After a short time the mercury begins to rise in the limb l, indicating that absorption has taken place, and if the heat be continued for several days the long tube will be nearly filled with mercury.
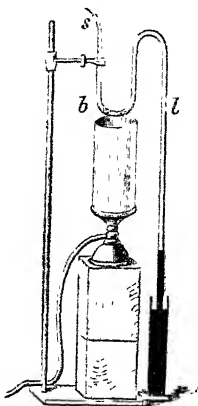
When sufficient absorption has taken place, withdraw the heat and break off the end s. The still alkaline substance at the bend is to be washed out with the least possible quantity of water, the liquid is rendered slightly acid with hydrochloric acid, a few drops of mercuric chloride are added, and the mixture is warmed. If the absorption of carbon monoxide in the tube has been considerable, the liquid will now become slightly turbid, owing to the reduction of

mercuric to mercurous chloride by formic acid, as in Experiment 700.

We can, therefore, effect the synthesis of formic acid, or rather of potassium formate, by direct union of carbon monoxide and caustic potash—

$$CO + HOK = H—COOK.$$
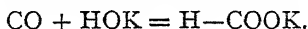
This synthesis was first effected by Berthelot.

Another synthesis of formic acid takes place when hydrocyanic acid is heated with caustic potash.

This reaction is obviously analogous to that already referred to, in which methyl cyanide affords potassium acetate and ammonia when heated with caustic potash. If, then, methyl cyanide be the nitrile of acetic acid, we must regard hydrogen cyanide as the nitrile of formic acid, or as *formonitrile*.

$$H—C \begin{array}{c} N + H_2 \\ + H \end{array} \begin{array}{c} O \\ OK \end{array} = H—C \begin{array}{c} O \\ OK \end{array} + NH_3.$$
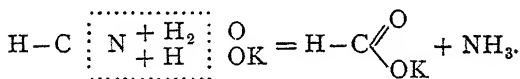
The acid can then be readily liberated from its potassium salt by the action of diluted sulphuric acid.

The list given on the next page includes the most important homologues of formic and acetic acids.

The higher numbers of this series are easily fusible solids which are insoluble in water, but, like the animal and vegetable fats, are easily dissolved by ether ; moreover, palmitic and stearic acids are the chief constituents of the natural fats, in which they occur as esters of a triatomic alcohol radical,[1] *glyceryl*, C_3H_5'''.

[1] The hydrate of this radical—$C_3H_5(OH)'_3$—is common *glycerine*.

Consequently, the whole series of homologues of acetic acid are generally termed the *fatty acids.*

Formic acid	.	.	$H - COOH$	boiling-point	99°C.
Acetic ,,	.	.	$CH_3 - COOH$	,, ,,	118°
Propionic ,,	.	.	$C_2H_5 - COOH$	,, ,,	140°
Butyric ,,	.	.	$C_3H_7 - COOH$	,, ,,	163°
Amylic (Valerianic)	.	.	$C_4H_9 - COOH$	,, ,,	184°
Caproic acid	.	.	$C_5H_{11} - COOH$	,, ,,	205°
Myristic acid	.	.	$C_{13}H_{27} - COOH$		
Palmitic ,,	.	.	$C_{15}H_{31} - COOH$		
Stearic ,,	.	.	$C_{17}H_{35} - COOH$	decomposed on	
Cerotic ,,	.	.	$C_{26}H_{53} - COOH$	distillation.	
Melissic ,,	.	.	$C_{29}H_{59} - COOH$		

Chlorides, anhydrides, &c., of many of the higher acids are known, and have been obtained by similar methods to those employed in the production of the acetic derivatives.

IV.

CHAPTER LI.

EXPERIMENTS WITH ALDEHYDE—ITS COMPOUNDS
WITH AMMONIA AND ACID SULPHITES. POLYMERS
OF ALDEHYDE—PARALDEHYDE—METALDEHYDE—
ALDOL — ETHIDENE COMPOUNDS. ALDOXIME—
ACETAL—CHLORAL—ITS HYDRATE—CHLOROFORM
—BROMOFORM—IODOFORM. OXIDATION OF THIO-
ALCOHOLS—SULPHONIC ACIDS. SULPHONES AND
SULPHINE COMPOUNDS.

IT has been already noted, in the course of Experiment 673, that an agreeable fruity odour is developed when ethyl alcohol, potassium bichromate, and diluted sulphuric acid are heated together, and it was found that a somewhat similar smell was produced when alcohol oxidises in contact with platinum black. In both cases it is no longer perceived when the alcohol is fully oxidised to acetic acid. The odorous body is an intermediate product of oxidation between the alcohol and the acid, and, when separated and analysed, is represented by the empirical formula, C_2H_4O. It is, therefore, alcohol *minus* two atoms of hydrogen, and is in consequence termed *aldehyde*.[1] Its formation is represented thus :—

$$C_2H_6O + O = C_2H_4O + H_2O.$$

$$\underbrace{}_{\text{Alcohol.}} \qquad \underbrace{}_{\text{Aldehyde.}}$$

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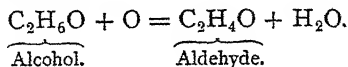
[1] Alcohol dehydrogenated.

We must now prepare a quantity of this body, and examine its properties, but it is desirable to use for this purpose a less energetic oxidising agent than potassium bichromate ; hence we shall employ manganese dioxide.

Experiment 703.—Place in a flask of 500 c. cs. capacity, and of the form shown in fig. 140, 60 grams of manganese peroxide in fine powder. Pour upon the powder a well-cooled mixture of 60 c. cs. of sulphuric acid, 40 c. cs. of strong spirit of wine, and 40 c. cs. of water. Agitate well, connect the flask with a good condenser, and surround the receiver with a freezing mixture. On the application of a gentle heat a very volatile, sweet-smelling liquid distils over ; this contains the aldehyde, mixed with some other bodies. When about 30 c. cs. have been collected the process may be stopped. The product is freely miscible with water, alcohol, and ether. With portions of this liquid make the following observations :—

(*a*) Note that a few drops, poured into a test-tube and gently warmed, rapidly volatilise. The boiling-point of pure aldehyde is 21·8, and the specific gravity of the liquid is 0·8.

(*b*) Add a few drops to solution of ammonia-nitrate of silver, in a test-tube, and heat. The tube becomes coated internally with a beautiful specular layer of *metallic silver*. The aldehyde, therefore, acts as a powerful *reducing* agent, and does so in consequence of its tendency to pass into *acetic acid* ; thus—

$$C_2H_4O + O = C_2H_4O_2.$$

G 2
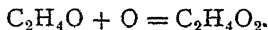
For the same reason, aldehyde, when exposed to the air, soon becomes *acid*.

(*c*) Add a few drops to some caustic potash, and warm the mixture in a test-tube ; a yellow colour is produced, and a peculiar resinous-looking body, termed *aldehyde-resin*, is formed.

(*d*) Mix 10 c. cs. with 20 c. cs. of pure dry ether, and saturate the mixture with dry ammonia gas. On standing, beautiful crystals of *aldehyde-ammonia*,

$$C_2H_4O,NH_3,$$
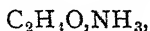
separate.

(*e*) Shake up 10 c. cs. with about 50 c. cs. of a nearly saturated solution of hydrogen sodium sulphite, $HNaSO_3$. On standing, crystals separate, which consist of

$$C_2H_4O,HNaSO_3.$$
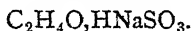
Pure aldehyde can be obtained either from aldehyde-ammonia or from the sulphite by heating the former with diluted sulphuric acid or the latter with sodium carbonate. The vapour is then dried by passing through warmed calcium chloride tubes, and condensed in a receiver surrounded with ice and salt.

Aldehyde affords three remarkable polymers. One of these, *Paraldehyde*, is a solid below 10° C. and boils at 124°. The specific gravity of its vapour accords with the formula—

$$C_6H_{12}O_3 = 3(C_2H_4O).$$
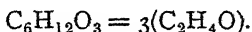
It is easily produced when aldehyde is mixed with a very small quantity of sulphuric acid.

Paraldehyde is soluble in about eight parts of water. It has been used as a hypnotic, *i.e.* for producing sleep; but its unpleasant taste and the uncertainty of its action have prevented its general employment.

The second polymer is termed *Metaldehyde*, and is produced when aldehyde is cooled in a freezing mixture and a little sulphuric acid added to it.

This is crystalline below $114°$, and it is insoluble in water. It is not known how many molecules condense to form metaldehyde.

Both modifications can be reconverted into aldehyde by distillation with a small quantity of sulphuric acid.

A third polymer was discovered by Wurtz, and is termed *Aldol*. It is formed when aldehyde is mixed with hydrochloric acid, diluted with twice its volume of water, and the mixture is allowed to stand for three days. A thick liquid is formed, which cannot be distilled under ordinary pressure without decomposition. Its molecule contains $C_4H_8O_2$.

When aldehyde is diluted with water, and sodium amalgam is added to the mixture, hydrogen unites with the aldehyde, and ethyl alcohol is reproduced—

$$C_2H_4O + 2H = C_2H_6O.$$
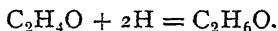
It is necessary to add a little hydrochloric acid from time to time, so as to neutralise the caustic soda formed.

Thus, by the addition of hydrogen on the one hand, or oxygen on the other, we can make aldehyde afford either alcohol or acetic acid. Having already ascertained the constitution of the two latter bodies,

the relations of aldehyde to them as a *transition* compound is shown by the following formulæ :—

Alcohol .	. .	$CH_3—CH_2—OH$
Aldehyde	. .	$CH_3—CO—H$
Acetic acid	. .	$CH_3—CO—OH$
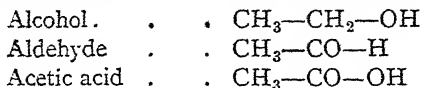
The homologues of ethyl alcohol afford aldehydes as first products of oxidation ; these bodies act as reducing agents, afford acids on oxidation, and combine with ammonia and acid sulphites, like acetaldehyde :

Alcohol.	Aldehyde.	Acid.
$H—CH_2—OH$	$H—CO—H$ [1]	$H—CO—OH$
$CH_3—CH_2—OH$	$CH_3—CO—H$	$CH_3—CO—OH$
$C_2H_5—CH_2—OH$	$C_2H_5—CO—H$	$C_2H_5—CO—OH$
$C_3H_7—CH_2—OH$	$C_3H_7—CO—H$	$C_3H_7—CO—OH$
&c.	&c.	&c.
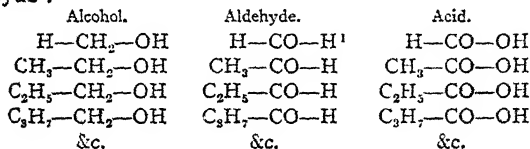
Just as the group —CO—OH is common to all the *acids*, so is —CO—H common to all *aldehydes*, and the latter group is readily converted into the former by oxidation. The *inverse change—i.e.* the reduction of the acid to its related aldehyde—is not so easily effected; but a mode of carrying out such a reduction through the anhydride was mentioned at page 73.

The formula for common aldehyde already given—
$$CH_3—CO—H$$
should obviously be written thus :—

$$CH_3—C{\overset{\displaystyle H}{\underset{\displaystyle O}{\big\langle}}}$$

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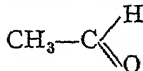
[1] Gaseous *methaldehyde*, COH_2, is obtained when a mixture of air with vapour of methyl alcohol is passed over a heated platinum spiral.

when a more detailed expression is required. So written aldehyde may be regarded as the oxide of the diad group $CH_3—CH''$, and this view is borne out by the fact that phosphorus pentachloride replaces the oxygen *only* by chlorine and forms *ethidene chloride*.

$$(CH_3—CH)''O \text{ becomes } (CH_3—CH)''Cl_2.$$
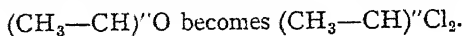
If any hydrogen were present as hydroxyl, it would have been removed along with the oxygen; the fact that it is not so removed is evidence that all hydrogen atoms are directly united to carbon.

On this view the constitution of the compounds of acid sulphites with aldehyde can be easily explained. The sodium compound can be written

$$(CH_3—CH)''\Big\langle{}^{OH}_{SO_3Na.}$$
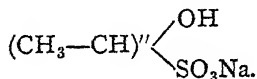
Similarly the compound formed by the union of aldehyde and ammonia is

$$(CH_3—CH)''\Big\langle{}^{OH}_{NH_2.}$$
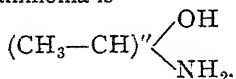
Again, hydroxylamine [1] can unite with aldehyde ; but in that case water is eliminated.

$$(CH_3—CH)''O + N'''{\Big\langle}{}^{OH}_{H}{}^{H} =$$

$$(CH_3—CH)''N'''—OH + H_2O.$$
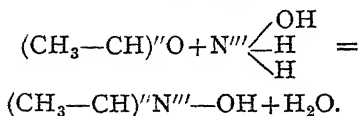
The product is termed *aldoxime*, or simply *oxime*,

[1] See part ii. p. 51, note.

and all the aldehydes afford compounds of the same kind, which were discovered by Victor Meyer.[1]

Dr. Maxwell Simpson, of Cork, has shown that hydrocyanic acid can unite with aldehyde and form the compound

$$(CH_3—CH)''\Big\langle{OH \atop CN,}$$
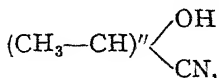
by means of which the synthesis of an important acid can be effected.   (See LACTIC ACID.)

Moreover, aldehyde acts in a peculiar way with alcohol, for when the two bodies are heated in a pressure tube to 100° a compound termed *Acetal* is produced, which is ethidene diethylate—

$$(CH_3—CH)''O + 2C_2H_5OH$$

$$= (CH_3—CH)''\Big\langle{OC_2H_5 \atop OC_2H_5} + H_2O.$$
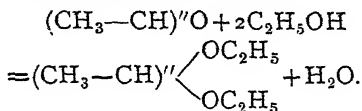
It is a colourless ethereal liquid boiling at 104° C. This body is produced in all cases of oxidation of alcohol ; thus the aldehyde obtained in the last experiment always contains some acetal ; and the latter contributes to the peculiar odour of the products formed, when alcohol is oxidised in presence of platinum black. Acetal is also formed during the action of chlorine on ethyl alcohol. We shall now examine this action experimentally.

Experiment 704.—Pass a current of chlorine gas through about 50 c. cs. of absolute alcohol ; place the flask containing the alcohol in water containing some

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[1] Aldehyde also combines with H_2S and affords a mixture of *thio-aldehydes*.

ice, if necessary, so that the temperature shall not rise above 10° C. The chlorine is absorbed, and after a short time *aldehyde* can be detected in the liquid when a few drops are removed, diluted with water, and heated with ammonia-nitrate of silver.[1] The primary action of the chlorine is therefore one of oxidation. If the current of gas be continued, a point is reached at which the liquid becomes turbid when a few drops are removed and diluted with water. The turbidity is due to the separation of *acetal*, which is almost insoluble in water. This body results from the action of the aldehyde first formed on the excess of alcohol, as already explained. If we stopped the operation at this point, it would be easy to separate the acetal formed. It is, however, of more interest to continue the treatment with chlorine; but the action must now be aided by heat.

Connect the flask with a condenser and gently warm the liquid to 60° C. while the current of chlorine is still maintained, and continue to pass the gas as long as any of it is absorbed. It is then boiled for a short time and allowed to cool, when it is cautiously mixed with an equal volume of strong sulphuric acid. Hydrochloric acid and some ethyl chloride are evolved, and the mixture is distilled from a water-bath. A colourless mobile liquid distils over, whose boiling point is 94·5° C. It reduces ammonia-silver nitrate like aldehyde, and forms crystalline compounds with acid sulphites : it generally acts like an aldehyde, but its formula is C_2Cl_3HO ; it is there-

[1] An excess of ammonia must be added in order to prevent the precipitation of chloride of silver.

fore trichloraldehyde, or simply *chloral*.[1]   Continued action of chlorine fails to replace the fourth atom of hydrogen ; the latter, therefore, occupies a different position in the molecule from the three replaced by chlorine, and this difference is exhibited in the structural formula—

$$CCl_3-C{<}^{H}_{O.}$$
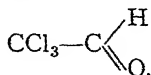
Chloral is oxidised to *trichloracetic* acid when heated with nitric acid, just as ordinary aldehyde is oxidised to acetic acid.   Moreover, nascent hydrogen reduces chloral to *aldehyde*.

The action of chlorine on absolute alcohol[2] can now be traced.   In the first stage *aldehyde* is formed ; then the aldehyde reacts with excess of alcohol, and *acetal* is produced ; next chlorine attacks the latter, and *trichloracetal* is ultimately formed.

$$(CCl_3-CH)''{<}^{OC_2H_5}_{OC_2H_5.}$$
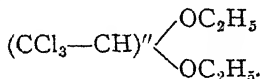
This product, when acted upon by the hydrochloric acid produced in the first stage of the reaction, affords ethyl chloride and *chloral ethylate* or alcoholate.

$$(CCl_3-CH){<}^{OH}_{OC_2H_5.}$$

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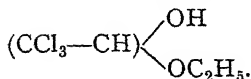
[1] Like ordinary aldehyde, chloral sometimes undergoes spontaneous polymerization and affords slightly soluble *meta-chloral*.

[2] Chloral is *not* formed when chlorine acts on aldehyde ; but a body termed *crotonchloral*—really the chloral of butylaldehyde, $C_4Cl_3H_5O$—is produced.

The alcoholate easily breaks up into *chloral* and alcohol under the influence of sulphuric acid. A number of secondary products are formed in the course of the above reactions, but it would be useless to attempt their isolation in the course of an experiment on a small scale.

If the chloral obtained be mixed with about one-fifth of its weight of water, the mixture gradually solidifies to a crystalline mass of *chloral hydrate*, which is very easily dissolved if more water be added. This substance is probably

$$(CCl_3-CH)''\Big\langle{}^{OH}_{OH}.$$
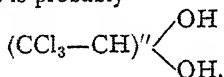
It melts at 57° C. and appears to boil at 98°, but actually decomposes into a mixture of chloral and water. All compounds which include two hydroxyls united to a single carbon atom are very unstable.

Chloral is not only easily soluble in water, but dissolves freely in alcohol and ether, and in four times its weight of chloroform. A curious liquid is obtained when solid chloral hydrate and *camphor* are rubbed together. The nature of the product is not known. Chloral, rich though it is in chlorine, does not part with the latter to caustic alkalies, but undergoes instead the change we shall now examine.

Experiment 705.—Dissolve in half a test-tube of water about half a gram of chloral or its hydrate ; next mix the liquid with a few drops of caustic soda solution. The mixture becomes milky, owing to the separation of minute droplets of a liquid ; these quickly unite and fall to the bottom of the tube, forming a

colourless fluid layer heavier than the solution in
which it has been formed. This liquid is *Chloroform,*
CCl$_3$H, while the solution in which it is produced
affords the characteristic reactions of sodium *formate.*
The equation explains the change [1]—

$$\overbrace{\text{NaO}\overbrace{\text{H} + \text{CCl}_3}}-\text{C}\!\!\underset{\text{O}}{\overset{\text{H}}{\diagdown}} = \text{CCl}_3\text{H} + \text{H}-\text{COONa}.$$
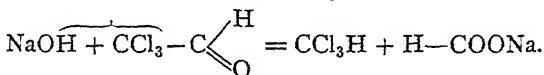
A knowledge of this change which chloral and its
hydrate suffer in presence of even very feebly alkaline
fluids led Liebreich to try the action of chloral hydrate
on animals, as he supposed that a similar decomposi-
tion would take place in the slightly alkaline blood,
and that the chloroform then formed would be free to
exert its well-known anæsthetic effects.   He thus
made the important discovery that chloral is a most
valuable hypnotic or sleep-producer ; but it is not
generally admitted that its action is due to the libera-
tion of chloroform in the blood.

We have already learned in the course of Experi-
ment 255 that chloroform is found among the pro-
ducts of the action of chlorine on marsh gas, and
that it is in fact trichlorinated marsh gas : very small
quantities of impure chloroform can be prepared in
that way.   On the other hand, chloroform can be
produced easily and in a state of great purity by the
action of an alkali on chloral hydrate ; but this
method involves the production and purification of

---

[1] The molecule of water in the hydrate is not represented
in the equation, as it is not concerned in the essential change,
being simply eliminated.   Chloral hydrate should give at least
70 per cent. of chloroform.

chloral, and is therefore expensive. Most of the chloroform used in surgery is, however, prepared by a process which probably involves the formation of chloral by the action of 'bleaching lime' on ethyl alcohol and subsequent decomposition by calcium hydrate. The ultimate change which takes place is represented by the equation—

$$4C_2H_6O + 8Ca(OCl)_2 = 2CCl_3H + 3Ca(OOCH)_2 + 5CaCl_2 + 8H_2O.$$
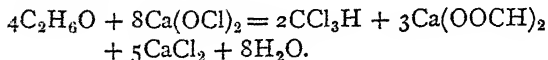
We can easily make a small quantity of chloroform by this method, which is that described in the British Pharmacopœia.

Experiment 706.—Introduce into a clean tin oil-can of four or five liters capacity 160 grams of good

FIG. 152.
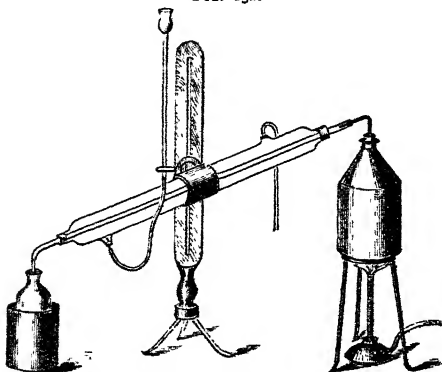
'chloride of lime' mixed with 80 grams of slaked lime; then pour in a mixture of 30 c. cs. of strong spirit of wine with half a liter of water; agitate the

contents of the vessel so as to secure complete mixture, and, having connected the can with a good condenser (as shown in fig. 152), apply a gentle heat. As soon as the liquid begins to distil over, withdraw the source of heat, and the action will continue unaided. When about 50 c. cs. have been collected in the receiver, which should be cooled by a freezing mixture, the operation is at an end.

Shake the distillate with its own volume of water, and let the heavy layer of chloroform subside ; then draw off the lighter liquid, and pour the rest into a separating funnel of the form shown in fig. 153. From this very useful piece of apparatus the chloroform can be drawn off free from water.

FIG. 153.

If required in a very pure state, the chloroform is shaken up for some time with an equal volume of strong sulphuric acid, then separated, washed with alkali, dried with solid calcium chloride, and distilled.

Chloroform, when pure, is a colourless liquid of specific gravity 1·52. It boils at 61° C. It dissolves in 200 parts of water, to which it communicates a peculiar sweetish taste, but is freely miscible with alcohol, ether, and many oils. It is an excellent solvent for fats, resins, iodine, and many other bodies.[1] Chloroform was discovered by Liebig in 1831. Its chief property, discovered by Sir J. Y. Simpson, of Edinburgh, is that of causing unconsciousness and insensibility to pain when inhaled.

The single atom of hydrogen in chloroform admits

[1] See note, page 119, for *Carbamine* test.

of replacement by various elements or groups. For example, when chlorine acts on chloroform in presence of some iodine, *Carbon tetrachloride* [1]—CCl_4—is produced; this is a liquid of specific gravity 1.62, which boils at $78°$; it has been used as an anæsthetic instead of chloroform. Again, when chloral is acted upon by fuming nitric acid, the compound $CCl_3(NO_2)$, termed *Chloropicrin*, is produced along with trichloracetic acid; this is a liquid of specific gravity 1.66 and boiling at $112°$; its vapour, which is extremely irritating to the eyes, readily explodes when superheated. Chloropicrin is also produced when *picric* acid (q.v.) in aqueous solution and bleaching lime are distilled together.

Bromal, CBr_3—COH, and its hydrate are also known, and are obtained by methods similar to those which afford the chlorine compounds. Bromal is an oily liquid whose specific gravity is 3.34, and boiling point is $173°$ C. By the action of alkalies it affords *Bromoform*—CBr_3H—which is a colourless liquid resembling chloroform in appearance. Its specific gravity is 2.77 and its boiling point $150°$ C. Like chloroform its hydrogen atom can be replaced by other elements or groups; thus it can afford *Bromopicrin* —$CBr_3(NO_2)'$—which resembles the corresponding chloropicrin in appearance, but its specific gravity is 2.81. When a small quantity of bromopicrin is rapidly heated in a test-tube, it decomposes and affords (in addition to carbon dioxide, oxides of nitrogen, and other bodies) *Carbon tetrabromide*—CBr_4—which is

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[1] Generally produced by the continued action of chlorine on CS_2 in presence of $SbCl_5$.

a white crystalline body melting at 91° and boiling at 189° (Groves); it undergoes partial decomposition near to its boiling point. *Iodal*, $CI_3 - COH$, has been obtained by the action of hydriodic acid on chloral or bromal; it boils above 200° C. *Iodoform*—CI_3H—is easily obtained directly from ethyl alcohol, as well as from many other bodies which contain the CH_3 group.

Experiment 707.—Dissolve 2 grams of crystallised sodium carbonate in 10 c. cs. of hot water; when the temperature has fallen to about 70° C., mix with 2 c. cs. of spirit of wine,[1] and add gradually with constant stirring a solution of 1 gram of iodine in about 3 grams of potassium iodide dissolved in a very small quantity of water. The colour of the iodine disappears, and a yellow powder soon separates, which is iodoform. The formation of the chief products is explained by the following equation :—

$$CH_3 - CH_2 - OH + 8I + 3Na_2CO_3 = CI_3H$$
$$+ HCOONa + 5NaI + 3CO_2 + 2H_2O.$$
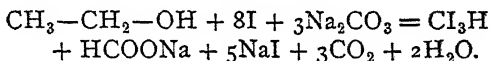
The iodoform, which is very slightly soluble in water, is collected on a filter and then dissolved in alcohol; when the alcoholic solution is evaporated, the iodoform can be obtained in fine yellow crystalline plates. Ether is also an excellent solvent of the compound.

Iodoform has a very characteristic odour. It melts at 119° and can be sublimed when cautiously heated; but it is easily decomposed at high temperatures.

The ease with which iodoform is produced from ethyl alcohol renders it an easy test for the latter.

[1] Pure methyl alcohol does *not* give iodoform.

Moreover, owing to the low solubility of iodoform in water, it serves as a delicate test, for 1 c.c. of spirit of wine in a liter of water can be easily recognised.

Experiment 708.—In order to apply the iodoform test for alcohol, rapidly distil 20 c.cs. of the liquid to be tested, add to the distillate a few drops of caustic soda solution and then iodine as long as it is decolourised. On standing, yellow plates of iodoform will deposit. As already stated, many other compounds than ethyl alcohol afford this iodoform reaction.

Carbon tetraiodide, CI_4, has been obtained in fine crystals which easily decompose into carbon and iodine. The compound CH_2I_2, *methylene iodide*, is produced by the action of hydriodic acid on iodoform.

The homologues of ethyl alcohol not only afford aldehydes, but several of the related chloraldehydes are known, as are their chlorinated and other derivatives allied to chloroform.

We have already pointed out that a sulphur analogue of ethyl alcohol is known—*Mercaptan* or *Thio-alcohol*, C_2H_5SH. When this body is oxidised by nitric acid it does *not* afford analogues of either aldehyde or acetic acid, but the SH group is oxidised to SO_2OH, and ethyl *sulphonic acid* is produced which affords numerous salts—

$$C_2H_5{-}SH + 3O = C_2H_5{-}SO_2{-}OH$$

$\underbrace{\phantom{C_2H_5{-}SH}}_{\text{Mercaptan.}}\qquad\underbrace{\phantom{C_2H_5{-}SO_2{-}OH}}_{\text{Ethyl sulphonic acid.}}$
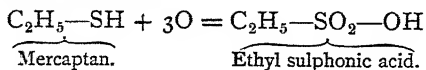
The homologues of ethyl mercaptan afford similar *sulphonic acids* on oxidation. The difference between a sulphonic and a sulphovinic acid will be readily

seen on comparing the formulæ of the ethylic compounds.

$$\begin{array}{c} C_2H_5O \\ HO \end{array}\!\!\Big>\!SO_2 \qquad\qquad \begin{array}{c} C_2H_5 \\ HO \end{array}\!\!\Big>\!SO_2$$

Sulphovinic acid.   Sulphonic acid.
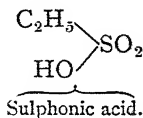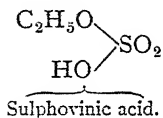
Ethyl sulphonic acid is metameric with ethyl hydrogen sulphite, but the sulphonic compounds are generally *much more stable bodies* than the metameric sulphites.

When ethyl sulphide—$(C_2H_5)_2S$—is oxidised, it affords the following bodies :—

$$\begin{array}{c} C_2H_5 \\ C_2H_5 \end{array}\!\!\Big\}\,SO \qquad \text{and} \qquad \begin{array}{c} C_2H_5 \\ C_2H_5 \end{array}\!\!\Big\}\,SO_2$$

Diethyl sulphoxide.   Diethyl sulphone.
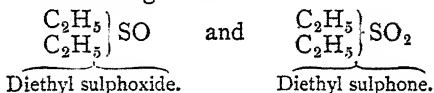
Thus the existence of ethyl sulphydrate and sulphide, and of their homologues, proves that sulphur and oxygen are interchangeable in many compounds without alteration of structure, when the sulphur acts as a diad ; but the sulphides are distinguished from the oxides of the alcohol radicals by the readiness with which they can form *addition compounds* such as diethyl sulphoxide and sulphone. They can also combine with methyl and ethyl iodides ; with the latter diethyl sulphide forms *triethylsulphine iodide*—

$$\begin{array}{c} C_2H_5 \\ C_2H_5 \end{array}\!\!\Big>\!S\!\Big<\!\begin{array}{c} C_2H_5 \\ I. \end{array}$$
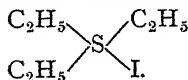
The production of these addition compounds is due to the fact that the sulphur atom can act as a tetrad, as well as a diad like oxygen.

CHAPTER LII.

ACETONE—ITS FORMATION AND RELATIONS—COM-
POUNDS WITH ACID SULPHITES—OXIMES—SYN-
THESIS—KETONES—THEIR DETECTION—ISOALCO-
HOLS—CARBINOLS—TESTS—ISOPARAFFINS.

In the course of Experiment 254 we found that a dry mixture of sodium acetate and soda-lime afforded, when heated, methyl hydride or marsh gas, and a metallic carbonate. We shall now examine the action of heat on an acetate which has not been mixed with any caustic alkali ; the particular salt we shall employ is *calcium acetate*, which does not easily fuse, and is therefore more convenient for our purpose than the sodium salt.

Experiment 709.—Add powdered chalk to 100 c.cs. of common acetic acid until a fresh addition does not cause any further effervescence ; the solution of calcium acetate thus formed is evaporated to complete dryness. The residue is powdered and, when perfectly dry, is to be introduced into a small retort whose beak is to be passed into a flask, which latter is cooled by partial immersion in water contained in a capsule, as shown in fig. 154. When carefully heated so as to effect the slow destructive distillation of the calcium acetate, a liquid condenses

in the neck of the retort and collects in the receiver.
The liquid condensed in the early stage of the opera-
tion is colourless, but it becomes coloured when the

FIG. 154.
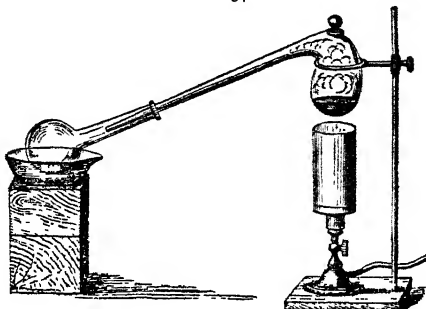
temperature is raised, as it must be towards the end
in order to complete the decomposition. When no
more liquid passes over, or only yellow oily drops
appear, the process may be stopped.

The residue in the retort is more or less charred,
and of course contains all the calcium, but chiefly as
carbonate, for a portion, when removed and treated
with an acid, effervesces strongly, owing to the evolu-
tion of carbon dioxide gas.

The liquid condensed in the flask has a peculiar
odour, unlike that of pure methyl alcohol, and it has
a burning taste; moreover, it easily burns with a
rather smoky flame. This liquid almost wholly con-
sists of a body which boils at 56·3°, and whose em-
pirical formula is C_3H_6O. This is termed *Acetone*.[1]

[1] Acetone is present in large amount in crude wood spirit.

Therefore, when dry calcium acetate is heated it is resolved into acetone and calcium carbonate. This is indicated in the following diagram :—

$$CH_3—CO—O—Ca''—O—CO—CH_3.$$
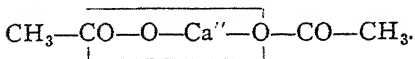
The general expression represents the constitution of calcium acetate as already ascertained ; the elements which form calcium carbonate—$CaCO_3$—are within the brackets, and when these are eliminated acetone —C_3H_6O—remains. But this mode of tracing the nature of the change leads us to form a definite conception of the structure of acetone itself, for it points to the existence of a simple relation between aldehyde and the new body, thus—

Aldehyde . . . $CH_3—CO—H$,
Acetone. . . . $CH_3—CO—CH_3$.
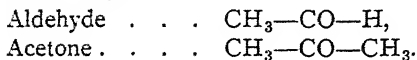
We have now to ascertain whether acetone resembles aldehyde in any particulars.

When we apply to the liquid the tests used in the case of the aldehyde, we find that it does *not* reduce ammonia silver nitrate ; it does *not* combine with ammonia under conditions similar to those which enable aldehyde and ammonia to unite, and it does *not* afford a single acid on oxidation ; but when heated with potassium bichromate and diluted sulphuric acid it yields *two* acids,[1] viz., acetic and formic, thus—

$$CH_3—CO—CH_3 + 3O = CH_5—CO—OH$$
$$+ HCO—OH,$$
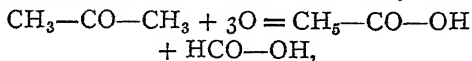
indicating that the molecule has broken up.

[1] As a matter of fact the formic acid generally undergoes further oxidation into carbon dioxide and water.

Two molecules of calcium carbonate, $CaCO_3$, and two of aldehyde, CH_3—CO—H, result.

Synthetic evidence of the structure of acetone has been obtained by Pebal and Freund, which completely confirms the conclusion at which we have already arrived. They found that a mixture of one molecule of zinc methide with two molecules of acetyl chloride, when allowed to stand for a few hours [1] and then treated with water, afforded acetone and zinc chloride—

$$2(CH_3—CO—Cl) + Zn(CH_3)_2 = ZnCl_2 + 2(CH_3—CO—CH_3).$$
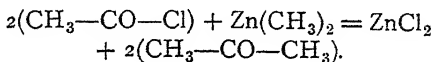
If in this reaction zinc ethide be substituted for the methide, the compound

$$CH_3—CO—C_2H_5$$

is obtained. Other radicals can be similarly introduced, and various acetones, or, as bodies of this class are generally termed, *ketones*, can be built up.

The calcium or barium salt of each of the fatty acids, when heated in the same way as calcium acetate, can afford a homologue of acetone. Thus calcium propionate affords *propione*, C_4H_8O ; calcium butyrate *butyrone*, $C_5H_{10}O$, and so on ; but as we ascend in the series, secondary products are obtained in large quantity and are difficult to separate.

Any of the above-mentioned calcium salts, when heated with calcium formate, can afford a corresponding aldehyde.

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[1] If several days are allowed to elapse before adding water, *trimethyl carbinol*—$(CH_3)_3C$—OH, is obtained. See p. 110.

Acetone and its homologues possess the remarkable property of uniting with mercuric hydrate in presence of free alkalies. This property, which was discovered and investigated by the writer, affords an easy and delicate method for the detection of acetone and certain other ketones.

Experiment 711.—To about half a test-tube of strong solution of mercuric chloride add a few drops of acetone, then mix with an excess of sodium hydrate solution, and warm if necessary. The yellow mercuric hydrate first precipitated by the alkali redissolves, and an alkaline liquid is obtained which is rich in mercury.

Divide the alkaline aceto-mercuric solution in two parts.

(*a*) Boil violently in a large test-tube, holding the mouth of the latter away from the person ; after some time a yellowish-white precipitate is formed. When the solution happens to be very strong, it thickens or coagulates on heating, like a solution of albumin or *white of egg.*

(*b*) To this add cautiously acetic acid so as to render the liquid faintly acid ; a whitish precipitate is obtained similar to the last.

The compound precipitated in each case consists of [1]

$$2 \ ((CH_3)_2CO)3HgO.$$
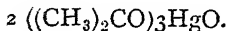
[1] When the alkaline solution is subjected to *dialysis* (see Experiment 551), free alkali and sodium chloride diffuse away, and a remarkable liquid is obtained which contains a hydrate of the aceto-mercuric compound in the *colloid state.*

The production of the aceto-mercuric solution¯ having the properties described above serves as a reliable test for acetones.

When aldehyde instead of acetone is present in the liquid from which mercuric hydrate is precipitated, the latter does *not* redissolve, but the precipitate gradually becomes greyish-white on heating.

We have already shown that aldehyde when treated with nascent hydrogen derived from sodium amalgam and water reproduces ethyl alcohol. When acetone is similarly treated it likewise combines with hydrogen, though much more slowly than does aldehyde under the same conditions.

When the liquid is distilled the chief product [1] is found to boil at 84° C., and its formula is C_3H_7OH. The presence of the hydroxyl group can be proved in the usual way, and numerous esters can be obtained from it ; it is therefore an *alcohol*.

But when we turn to the list of alcohols on page 37 it is noted that the above-mentioned body differs materially in boiling-point from the tricarbon (propyl) alcohol : the latter boils at 98° C., whereas the propyl alcohol obtained by the addition of hydrogen to acetone boils at 84° C. These two distinct compounds contain the same elements in the same proportions, and their molecular weights are the same. They are therefore *metameric alcohols.*

It is evident that the differences in properties between the two alcohols must be due to difference

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[1] Another body termed *pinacone*, $(CH_3)_4C_2H_2(OH)_2$, is formed at the same time.

of chemical structure. We have therefore to examine the evidence of constitution obtainable in each case ; and the question is obviously narrowed to the structure of the group C_3H_7, as we have already seen that both contain hydroxyl.

The liquid which boils at 98° C. is called 'normal propyl alcohol,' because it can be built up by methods similar to those already pointed out in the case of ethyl alcohol. That is to say, while the synthesis of *ethyl* alcohol can be effected with the aid of *methyl* compounds, and the structure of ethyl, C_2H_5, can be shown to be CH_3-CH_2, propyl alcohol can be derived from *ethyl* compounds, and the structure of propyl, C_3H_7, can be shown to be $C_2H_5-CH_2-$. This view is confirmed by the study of the oxidation of the alcohols.

$$H-CH_2-OH \quad . \quad . \quad \text{becomes} \quad . \quad . \quad H-CO-OH.$$
$$CH_3-CH_2-OH \quad . \quad . \quad \text{,,} \quad . \quad . \quad CH_3-CO-OH.$$
$$C_2H_5-CH_2-OH \quad . \quad . \quad \text{,,} \quad . \quad . \quad C_2H_5-CO-OH.[1]$$
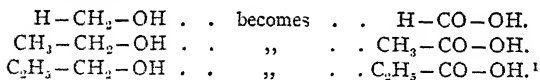
If, then, ethyl be CH_3-CH_2-, the full expression for normal propyl alcohol is

$$CH_3-CH_2-CH_2-OH.$$
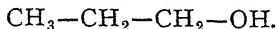
We now turn to the liquid that boils at 84° C., or 'isopropyl alcohol,' which is obtained by the addition of two atoms of hydrogen to acetone. When that alcohol is oxidised, *propionic acid is not formed, but acetone is reproduced*. The acetone structure therefore persists in isopropyl alcohol, and, as we have already

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[1] Propionic acid is formed when *ethyl cyanide* is heated with alkalies or acids.

seen, the peculiarity of that structure is the direct
linkage of the carbon of two methyl groups to the
third carbon atom, which latter is also directly united
to oxygen ; hence the constitution of isopropyl alcohol
is represented by the formula—

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!\!\Big\rangle CH\!-\!OH$$
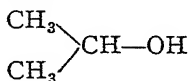
The formation of acetone—

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!\!\Big\rangle CO$$
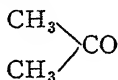
from it by removal of two atoms of hydrogen by oxi-
dation is therefore perfectly intelligible.

The recognition of these two distinct but meta-
meric propyl alcohols led the late Professor Kolbe of
Leipzig to formulate his 'carbinol' theory.   On this
view methyl alcohol is the typical compound of which
all the higher alcohols are substitution products ; that
body he termed *carbinol*, and wrote its formula thus—

$$\begin{matrix} H \\ H \\ H \end{matrix}\!\!\!\Big\rangle C\!-\!OH.$$
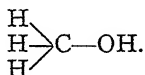
The first alcoholic derivative of this is ethyl alcohol,
which is obviously *methyl carbinol*—

$$\begin{matrix} CH_3 \\ H \\ H \end{matrix}\!\!\!\Big\rangle C\!-\!OH.$$
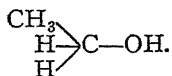
No isomers of ethyl alcohol are known, and they

are impossible if we assume that the three hydrogen atoms directly united to carbon in the carbinol are of equal value, and all the evidence we possess points to that conclusion. Isomerism only becomes possible when a tricarbon alcohol is concerned. Normal propyl alcohol is *ethyl carbinol*—

$$\left. \begin{array}{c} C_2H_5 \\ H \\ H \end{array} \right\rangle C\text{---}OH$$
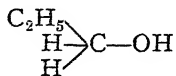
and isopropyl alcohol is *dimethyl carbinol*—

$$\left. \begin{array}{c} CH_3 \\ CH_3 \\ H \end{array} \right\rangle C\text{---}OH.$$
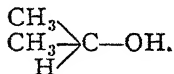
As we have already developed the structure of ethyl ($CH_3\text{---}CH_2\text{---}$), it will be readily seen that in the normal alcohol *but one* carbon atom can be directly united to that of the carbinol, which we shall in future call the 'nucleus.' This is true of all normal alcohols, which are therefore said to be *primary*, as they are products of the replacement of but one atom of hydrogen in the carbinol. When two atoms of hydrogen are replaced, as in the case of the isopropyl compound, the alcohol is said to be *secondary*, and here two carbon atoms are directly united to that of the nucleus.

It is evident that no more than two propyl alcohols are possible, and only two are known. But *four* metameric butyl alcohols exist according to theory, and all are known. Two of these are primary, viz., *normal*

propyl carbinol, which boils at 116°, and *isopropyl carbinol*,[1] whose boiling-point is 109°,

$$\begin{matrix} C_3H_7 \\ H \\ H \end{matrix} \!\!> C-OH \quad \text{and} \quad \begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!> \begin{matrix} CH \\ H \end{matrix} \!\!> C-OH.$$
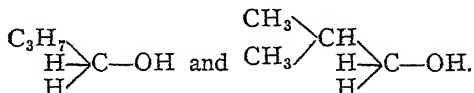
One secondary alcohol, or *ethyl methyl carbinol*,[2] boiling-point 99°,

$$\begin{matrix} C_2H_5 \\ CH_3 \\ H \end{matrix} \!\!> C-OH,$$
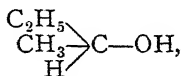
and one tertiary alcohol, or *trimethyl carbinol*,[3] boiling-point 82·5°,

$$\begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix} \!\!> C-OH.$$
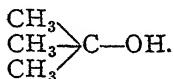
It is evident, then, that the following carbinol residues are characteristic :—

$-CH_2-OH$ of primary alcohols,
$=CH-OH$ „ secondary „
$\equiv C-OH$ „ tertiary „
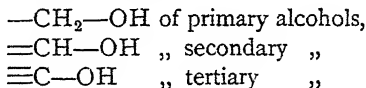
It is important to have a ready means of practically distinguishing between these classes of isomeric alcohols, and this is supplied by Meyer's method. This consists in (*a*) converting the alcohol into its iodide

---

[1] On oxidation these bodies give two metameric butyric acids.

[2] On oxidation this affords ethyl-methyl ketone.

[3] On oxidation does not give corresponding acid containing the same number of atoms of carbon, nor does it afford a ketone.

by distillation with PI_3 ; (*b*) the iodide is then heated in a test-tube with silver nitrite, by which means it affords a nitroparaffin (see Experiment 683) ; (*c*) the latter is warmed with an alkaline solution of potassium nitrite, and diluted sulphuric acid is slowly added to the mixture. If the alcohol be tertiary, no colour change is observed. If secondary a *blue* liquid is produced, because nitrous acid acts on such a nitroparaffin as that derived from secondary butyl alcohol, and an atom of hydrogen is replaced by the group NO, forming a *pseudonitrol*, and the solutions of all such bodies are blue.

$$\begin{matrix} C_2H_5 \\ CH_3 \\ H \end{matrix}\!\!>\!\!C\!\!-\!\!NO_2 \qquad\qquad \begin{matrix} C_2H_5 \\ CH_3 \\ NO \end{matrix}\!\!>\!\!C\!\!-\!\!NO_2$$
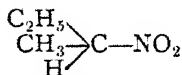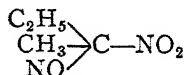
Nitroparaffin (2nd).   Pseudonitrol.

The nitroparaffin of a primary alcohol affords a *red* colour under similar conditions, because nitrous acid produces a *nitrolic acid*, whose alkaline salts are red in colour.

$$\begin{matrix} C_3H_7 \\ H \\ H \end{matrix}\!\!>\!\!C\!\!-\!\!NO_2 \qquad\qquad \begin{matrix} C_3H_7 \\ \\ HO\!\!-\!\!N \end{matrix}\!\!>\!\!C\!\!-\!\!NO_2$$
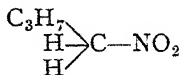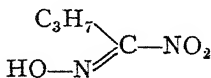
Nitroparaffin (1st).   Nitrolic acid.

Having recognised the existence of groups of metameric alcohols, we should expect to find somewhat analogous groups of metameric *paraffins*, and many such have been investigated.

The normal and isoparaffins may be regarded as marsh gas or methane derivatives, just as the normal and isoalcohols are substituted carbinols. The first

three paraffins have no isomers, nor are any possible.

$$
\left.\begin{array}{l} H \\ H \\ H \\ H \end{array}\right\} C \quad : \quad \left.\begin{array}{l} CH_3 \\ H \\ H \\ H \end{array}\right\} C \quad : \quad \left.\begin{array}{l} C_2H_5 \\ H \\ H \\ H \end{array}\right\} C \ \text{or} \ \begin{array}{l} CH_3 \\ CH_2 \\ CH_3 \end{array}
$$

Methane.   Ethane.   Propane.
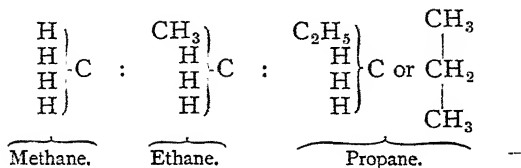
Isomerism begins at the four carbon paraffins. Only two tetranes are possible, and they are known.

$$
\left.\begin{array}{l} C_3H_7 \\ H \\ H \\ H \end{array}\right\} C \ \text{or} \ \begin{array}{l} CH_3 \\ CH_2 \\ CH_2 \\ CH_3 \end{array} \quad : \quad \left.\begin{array}{l} CH_3 \\ CH_3 \\ CH_3 \\ H \end{array}\right\} C
$$

Normal or diethyl.   Iso- or
                                 trimethylmethane.
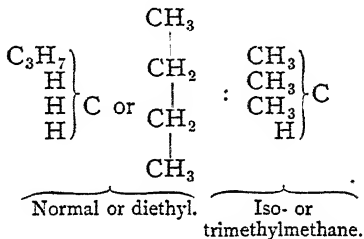
As the number of carbon atoms increases the number of possible and known isomers increases; but the normal paraffins are the most important, as they are the most stable, and they alone afford normal alcohols. The detailed study of the metameric alcohols and related paraffins should be reserved for a later stage of the student's course.

CHAPTER LIII.

ACETAMIDE—RELATED BODIES : CYANIDES AND ISO-
CYANIDES OF ALCOHOL RADICALS—CYANATES AND
ISOCYANATES — AMINES AND AMMONIUM DERI-
VATIVES—THEIR DISCRIMINATION—HYDRAZINES
—TETRAZONES—PHOSPHORUS, ANTIMONY, AND
ARSENIC BASES—CACODYL DERIVATIVES : BORON
AND SILICON COMPOUNDS WITH METHYL AND
ETHYL.

WE now know that ketones are obtained when the calcium salts of acetic acid, or of its higher homologues, are heated alone. The corresponding compounds of barium, or of several other metals, may be substituted for those of calcium in the operations referred to without material change in the nature of the products of decomposition, but if we use the *ammonium* salts bodies of a new kind result.

Experiment 712.—Neutralise about 200 c.cs. of strong acetic acid with ammonia, so as to produce a solution of ammonium acetate. Introduce it into a retort provided with a thermometer, and rapidly distil. At first water only passes over, then an acid liquid, and finally, when the boiling-point has risen above 200°, a colourless oily liquid, which should be separately

collected. The latter on standing slowly solidifies to a mass of crystals. This substance consists of

$$CH_3—CO—NH_2,$$

and obviously results from the loss of a molecule of water by ammonium acetate—

$$CH_3—CO—ONH_4.$$
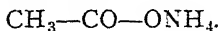
The new body is termed *acetamide*, and may be regarded as a derivative of acetic acid in which the hydroxyl of the acid has been replaced by the monad group, NH_2, or amidogen. Bodies of this kind are generally termed *amides*.

Acetamide melts at 78°, and boils at 222°; its vapour has a smell of mice. It is readily dissolved by water and alcohol, but does not dissolve in ether unless the latter contains alcohol. If hydrochloric acid gas be passed into a solution of acetamide in a mixture of alcohol and ether, a compound separates which consists of

$$(CH_3—CO—NH_2)_2HCl.$$
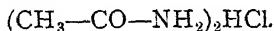
In this case the amide acts as a very feeble *basic* body towards hydrochloric acid.

Acetamide is easily produced by other methods, *e.g.* by the action of ammonia on acetyl chloride—

$$CH_3—CO—Cl + 2NH_3 = CH_3—CO—NH_2 + \\ NH_4Cl.$$
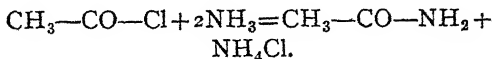
And by the continued action of ammonia on ethyl acetate—

$$CH_3—CO—OC_2H_5 + NH_3 = CH_3—CO—NH_2 + \\ HO—C_2H_5.$$
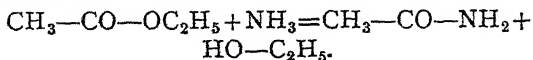
The homologues of acetamide are obtained by similar methods.

It is obvious that the removal of the elements of water from acetamide should afford *methyl cyanide* or acetonitrile.

Experiment 713.—Put two or three grams of dry acetamide in a test-tube, provided with a cork and bent tube that can be connected with a condenser, and cover the solid with a thick layer of phosphoric anhydride, P_2O_5. Heat gently to start the action; some liquid soon distils over, which boils at $82°$; this is *methyl cyanide*—

$$CH_3—CO—NH_2 + P_2O_5 = CH_3—CN + 2HPO_3.$$
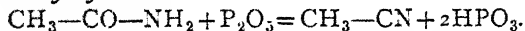
This is one of the most convenient methods that can be adopted for the preparation of the cyanide. It is not absolutely necessary to prepare acetamide in the first instance, since ammonium acetate, when treated with a large excess of phosphoric anhydride, will also afford the cyanide.

The converse change can be effected, for the cyanide, when heated to $180°$ with water in a pressure tube, will afford acetamide first and ammonium acetate by continued action. One molecule of water only is required to convert methyl cyanide into acetamide—

$$CH_3—CN + H_2O = CH_3—CO—NH_2.$$
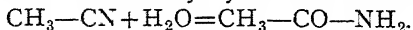
If acetic acid be used instead of water, and the mixture be heated to $230°$, a new body is formed—*diacetamide*—which boils at $215°$, and is a crystalline solid below $75°$—

$$\begin{matrix} CH_3—CN \\ + \\ CH_3—CO—OH \end{matrix} = \begin{matrix} CH_3—CO \\ \\ CH_3—CO \end{matrix} \Big\rangle NH.$$
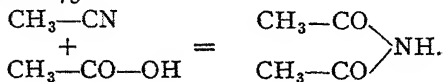
This body, unlike acetamide, possesses distinct *acid* characters. When methyl cyanide is heated to 200° with acetic anhydride, *triacetamide* is obtained, which is a *neutral* crystalline solid below 79°—

$$CH_3-CN$$
$$+$$
$$CH_3-CO\diagdown \qquad CH_3-CO\diagdown$$
$$\qquad\qquad O = CH_3-CO\rightarrow N.$$
$$CH_3-CO\diagup \qquad CH_3-CO\diagup$$
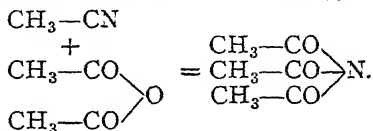
It is evident that triacetamide may be viewed as ammonia, H_3N, in which all three hydrogen atoms have been replaced by the oxidised group acetyl; it is said to be a *tertiary* amide. Diacetamide is a *secondary* amide, and acetamide *primary*.[1]

Viewed from a somewhat different standpoint, we can recognise the following ammonia residues in these compounds :—

—NH_2 monad, or *amide* as in acetamide.
=NH diad, or *imide* „ diacetamide.
≡N triad, or *nitrile* „ triacetamide.

The cyanide may also be regarded as a nitrile compound.

Methyl cyanide, or *acetonitrile* (see page 68), is a colourless liquid of specific gravity 0·79. It has a rather agreeable odour, and is almost non-poisonous.[2] The boiling-point of methyl cyanide is 82°.

Its formation from acetamide, and the readiness with which it reproduces acetamide by union with

---

[1] The hydrogen in primary and secondary amides can also be replaced by alcohol radicals (see page 125).

[2] It may easily contain a highly poisonous impurity—an isocyanide (see page 119). Hence it should not be inhaled.

one molecule of water, or ammonium acetate with two molecules of water, lead us to conclude that the carbon of the methyl group is united to the carbon of the cyanogen—in other words, that it includes the system $CH_3—C≡$. The formation of acetic acid from the cyanide by heating with caustic alkalies or *with hydrochloric acid* is evidence in the same direction. Further proof of this important point is obtained by the study of the action of nascent hydrogen on the cyanide.

Experiment 714.—Dilute about 5 c.cs. of sulphuric acid with about 50 c.cs. of water, and add about 1 c.c. of methyl cyanide. The latter mixes readily ; then add a considerable excess of granulated zinc. Some hydrogen gas is evolved, but a portion of the hydrogen displaced by the zinc does not appear as gas, as it attaches itself to the cyanide. When no more zinc dissolves, pour off the liquid, add excess of caustic soda to it, and boil. A distinct *ammoniacal* odour is perceived, and the vapour restores the blue colour of litmus paper previously reddened by an acid. Therefore an *alkaline* body like ammonia is evolved.

The alkaline vapour so produced has been collected and examined, and has been found to contain a powerfully basic body represented by the formula $CH_3—CH_2—NH_2$.

By the action of nascent hydrogen on methyl cyanide, therefore, the system $CH_3—C≡$ has been changed into $CH_3—CH_2—$ or ethyl, by addition of hydrogen, while the nitrogen of the cyanide has also combined with hydrogen, and the amidic group, NH_2,

is another product.[1]   The new body is *not* named
ethylamide, but is termed *ethylamine.*   Its relation to
ammonia may obviously be thus shown—

$$\left.\begin{matrix} H \\ H \\ H \end{matrix}\right\}N \qquad : \qquad \left.\begin{matrix} C_2H_5 \\ H \\ H \end{matrix}\right\}N.$$
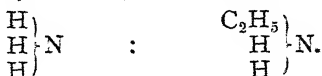
When *unoxidised radicals,* like C_2H_5, take the
place of hydrogen in ammonia, the product is termed
an *amine,* as above 'ethylamine;' the terminal *amide*
being reserved for the cases in which an *oxidised
radical,* such as acetyl, CH_3—CO, replaces the hydro-
gen, as in *acetamide.*

Nitroethane, $C_2H_5NO_2$, can be reduced by nascent
hydrogen to ethylamine, and the latter can be formed
in other ways ; moreover, ammonia derivatives exist,
including two and three ethyl groups.

Methyl cyanide is not only producible by the
dehydration of acetamide ; it is also formed when
ordinary potassium cyanide is distilled with methyl
hydrogen sulphate—

$$KCN + CH_3HSO_4 = CH_3CN + KHSO_4.$$
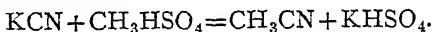
In this reaction a small proportion of a strong-
smelling liquid is obtained, along with the true
cyanide of methyl.   This body is metameric with the
cyanide, but is distinguished from it not only by its
odour, but by its boiling-point, which is 58° (that of
the cyanide being 82°), and other characters ; it is
termed *methyl isocyanide,* or methyl *carbamine,* for a
reason that will presently appear.   As already pointed

[1] This reaction obviously enables us to pass up the series
from mono- to di-carbon compounds.

out (page 39), methyl isocyanide is the chief product of the action of methyl iodide on silver cyanide.

The isocyanide is not only distinguished from the cyanide of methyl by its odour and lower boiling-point, but also by the following characters.

(*a*) It does *not* hydrate to acetamide, nor is it attacked by caustic potash under the same conditions as the cyanide.

(*b*) It is acted on by hydrochloric acid, but affords different products from the cyanide, viz., formic acid and *methylamine*, CH_3NH_2. This reaction is significant of the structure of the isocyanate, for it indicates that the two carbon atoms are not directly united, as in the cyanide, but are connected by means of triad nitrogen, thus—

$$CH_3-N = C\diagup_{\diagdown}$$
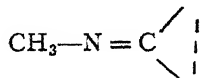
The carbon atom not engaged with hydrogen is obviously in an unsaturated condition and is easily detached ; hence the formation of formic acid on hydration in presence of hydrochloric acid [1]—

$$CH_3-N=C + 2H_2O = CH_3-NH_2 + HCOOH.$$

[1] The inverse change—*i.e.* the conversion of a primary amine into an isocyanide or carbamine—is easily effected by heating the amine or a salt of it with *chloroform* and caustic potash. In the case of methylamine the following reaction occurs :—

$$CH_3NH_2 + CHCl_3 + 3KOH = CH_3NC + 3KCl + 3H_2O.$$
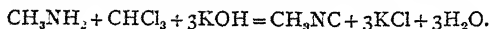
The offensive odour of the carbamine, CH_3NC, is easily recognised. If a methylamine salt be not obtainable, a primary

All the operations hitherto performed with methyl isocyanide lead to the same conclusions as to its structure. The term *carbamine*, or carbylamine, refers to the fact that an atom of carbon occupies a similar place in the compound to the two atoms of hydrogen in the NH_2 group of methylamine.

The presence of an unsaturated carbon atom in the isocyanide should render it a *reducing* agent, and it does so act when warmed with mercuric oxide; metallic mercury and methyl *isocyanate* result—

$$CH_3—N=C + HgO = CH_3—N=C=O + Hg.$$
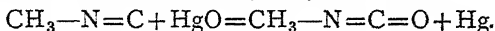
Methyl isocyanate is a colourless liquid which boils at 44°. It is formed when methyl potassium sulphate is distilled with potassium cyanate (see Part II., p. 207); hence it would appear that the latter is an isocyanate. It is also produced when methyl iodide and silver cyanate are heated together. Hence ordinary silver cyanate and cyanide are probably iso-compounds themselves.

The higher isocyanates are prepared by similar methods, and resemble the methyl compound in properties.

True methyl cyanate, $CH_3—O—CN$, is obtained by the action of cyanogen chloride on sodium methylate; this mode of formation indicates its structure—

$$CH_3—ONa + ClCN = NaCl + CH_3—O—CN.$$
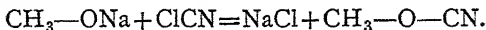
amine of another series—*aniline*, $C_6H_5NH_2$, which can be readily purchased—may be used instead—

$$C_6H_5NH_2 + CHCl_3 + 3KOH = C_6H_5NC + 3KCl + 3H_2O.$$
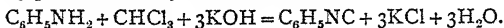
This carbamine reaction serves as a convenient *test for chloroform.*

It is a yellow oily liquid which easily polymerises, forming methyl cyanurate.

The homologues of methyl cyanate are formed in similar reactions.

Thiocyanates and isothiocyanates of alcohol radicals are also known, and will be referred to later on.

The late Professor Wurtz discovered the important group of bodies now termed *amines*, and his method of producing them consists in boiling the isocyanate of the alcohol radical with caustic potash, when it is broken up into a primary amine and potassium carbonate. Thus methyl isocyanate affords *methylamine*—

$$CH_3-N=CO+2HOK=CH_3-NH_2+CO(OK)_2.$$
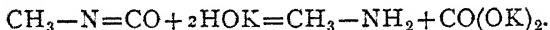
Ethyl isocyanate gives *ethylamine* [1]—

$$C_2H_5-N=CO+2HOK=C_2H_5-NH_2+CO(OK)_2.$$
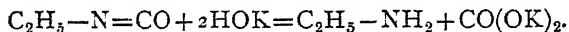
It is also possible to prepare primary amines from acetamide and its homologues by means of a very interesting reaction recently described by Dr. Hofmann.

Experiment 715.—Introduce 16 grams of bromine into a flask, and add 6 grams of acetamide; when the latter is completely dissolved, add 5·6 grams of caustic potash (*not* soda) dissolved in 100 c.cs. of water. Mix, and allow to stand for a short time. The following changes occur :—

$$CH_3-CO-NH_2+2Br+KOH=$$
$$CH_3-CO-NHBr+KBr+H_2O.$$
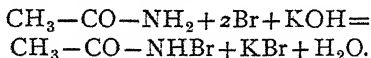
[1] The body already formed by the action of nascent hydrogen on acetonitrile (see page 117).

It is possible to separate the *bromacetamide* from the solution, but it is unnecessary to do so for our purpose. Now add 17 grams of caustic potash dissolved in 50 c.cs. of water; connect the flask with a condenser and rapidly distil. A strongly alkaline vapour, consisting of a mixture of methylamine and ammonia, passes over, which is received in a flask containing 20 c.cs. of strong hydrochloric acid. When the liquid which distils over is no longer alkaline to test paper, the process may be stopped. The bromacetamide breaks up in the following way :—

$$CH_3-CO-NHBr+3KOH=CH_3NH_2+CO(OK)_2$$
$$+KBr+H_2O.$$
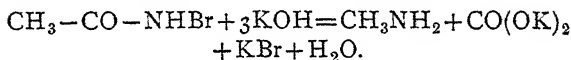
The liquid in the receiver contains a mixture of methyl ammonium and ammonium chlorides. Evaporate to dryness on the water bath, and digest the solid residue[1] with absolute alcohol, which dissolves the methyl compound and leaves the ammonium chloride undissolved. When the alcoholic solution is filtered off and evaporated to a small bulk, crystals of methylammonium chloride are obtained.

It has been already pointed out that methylamine and ethylamine are primary amines; these bodies are related in the following way to ammonia, and, like the latter, are powerful bases.

$$\left.\begin{array}{c}H\\H\\H\end{array}\right\}N \quad : \quad \left.\begin{array}{c}CH_3\\H\\H\end{array}\right\}N \quad : \quad \left.\begin{array}{c}C_2H_5\\H\\H\end{array}\right\}N.$$

Ammonia.   Methylamine.   Ethylamine.
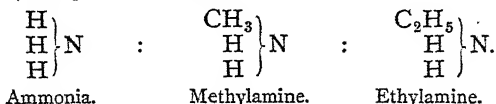
[1] If some of this be heated in a test-tube with caustic potash, methylamine is given off, which *can be burned at the mouth of the tube.*

As in the analogous cases of the amides it should be possible to replace the remaining hydrogen atoms in succession. That is to say, just as we can form di- and tri-acetamide, so should we be able to produce this series—

$$\left.\begin{array}{c}C_2H_5 \\ H \\ H\end{array}\right\}N \quad : \quad \left.\begin{array}{c}C_2H_5 \\ C_2H_5 \\ H\end{array}\right\}N \quad : \quad \left.\begin{array}{c}C_2H_5 \\ C_2H_5 \\ C_2H_5\end{array}\right\}N.$$

Ethylamine.   Diethylamine.   Triethylamine.
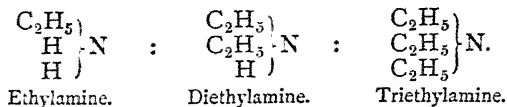
These substituted ammonias can be formed in succession by a line of treatment also due to Dr. Hofmann. This consists in the action of excess of the iodide of the alcohol radical, *e.g.* ethyl iodide, on alcoholic solution of ammonia.

Experiment 716.—Saturate 20 c.cs. of nearly absolute ethyl alcohol with dry ammonia gas, and mix it with 5 c.cs. of ethyl iodide. Seal the mixture in a stout pressure tube (fig. 155), and, having wrapped it up in a cloth, heat in a water-bath for two or three hours. Or the mixture may be heated in one of the small stout bottles in which 'lithia water' is often sold ; the cork can be wired down. In any case the temperature should be gradually raised to the boiling-point of water, and when the operation is at an end, after about two hours, the tube or bottle should be allowed to cool slowly to the ordinary temperature before opening. The contents are poured into a capsule and evaporated to dryness over the water-bath. The saline residue left consists of the iodides in the following list, and when the mixture is

FIG. 155.
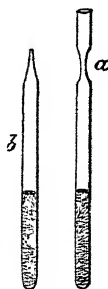
distilled from a retort with strong potash solution, the
bases are set free which are indicated, together with
their boiling-points, in the parallel columns.

H_4NI	gives	$H_3N.$	—
$(C_2H_5)H_3NI$	,,	$(C_2H_5)H_2N.$	$+19°$
$(C_2H_5)_2H_2NI$	,,	$(C_2H_5)_2HN.$	$57·5°$
$(C_2H_5)_3HNI$	,,	$(C_2H_5)_3N.$	$91°$
$(C_2H_5)_4NI$	not decomposed.		

The last-named compound remains behind in the
retort, the bases pass over into the receiver, which
should contain some hydrochloric acid ; here they at
once form chlorides. When the solution from the
receiver is evaporated to dryness and the residue is
digested with strong alcohol, ammonium chloride is
left behind, while the chlorides of the ethyl bases
dissolve, and can then be obtained in the solid form
by distilling off the alcohol. The separation of the
ethyl bases from one another [1] is a difficult operation,
and is effected by acting on the free bases with ethyl
oxalate. Triethylamine is not acted on by the oxalate,
and can be distilled off. The oxalate affords a crys-
talline compound with ethylamine and an oily liquid
with diethylamine ; these products are mechanically
separated, and each is then distilled with potash, by
which means the free bases are obtained. The action
of oxalic ether on ethylamine and diethylamine will
be explained later on (*see* OXAMIDE).

Ethylamine $(C_2H_5)H_2N.$ This is a colourless,

---

[1] Though there is a wide difference in boiling-point between
the amines, they cannot be separated by fractional distillation
alone.

mobile, and very volatile liquid, which boils at 19°. It has a strong ammoniacal odour and alkaline reaction. Its vapour burns with a yellowish flame. The basic power of ethylamine is greater even than that of ammonia, as the latter can be displaced from its compounds by the amine. It precipitates aluminum hydrate, but, unlike ammonia, it redissolves the precipitate. On the other hand it does *not* redissolve cadmium hydrate, and slowly dissolves copper hydrate. With chloroplatinic acid it gives the salt $(N(C_2H_5)H_3)_2PtCl_6$, which resembles the ammonium salt $(NH_4)_2PtCl_6$ in composition.

Diethylamine, $(C_2H_5)_2HN$, is a colourless and powerfully alkaline liquid, readily forming salts [1] like ethylamine, but boils at 57·5°. It is also combustible. Like ethylamine it redissolves aluminum hydrate, but cupric hydrate is scarcely soluble in it.

Its platinum salt contains $[N(C_2H_5)_2H_2]_2PtCl_6$.

Triethylamine, $(C_2H_5)_3N$, is a liquid which boils at 91°, and, like the two preceding bodies, is a powerful base ; unlike them it is only slightly soluble in water. Its platinum compound contains

$$[N(C_2H_5)_3H]_2PtCl_6.$$
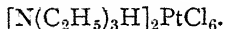
When triethylamine and ethyl iodide are mixed, they slowly combine and form a crystalline body

---

[1] Ethylated amides are easily obtained by heating these amine salts. Thus *ethyl acetamide* results on heating ethyl ammonium acetate—

$$CH_3CO—ON(C_2H_5)H_3 = CH_3—CO—N(C_2H_5)H + H_2O,$$
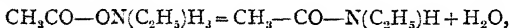
and diethyl acetamide from diethyl ammonium acetate—

$$CH_3CO—ON(C_2H_5)_2H_2 = CH_3—CO—N(C_2H_5)_2 + H_2O.$$
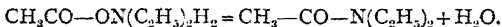
which contains $N(C_2H_5)_4I$. This is the iodide of the *ammonium base* or *iodide of tetrethylammonium*. The same body is formed along with the other iodides by the action of excess of ethyl iodide on ammonia, but, as already pointed out, it is *not* decomposed by potash. The iodide is soluble in water, and when to its solution moist silver oxide is added, silver iodide is formed and a powerfully alkaline liquid is obtained. When the mixture is filtered and carefully evaporated, a deliquescent mass remains, which contains the hydrate $N(C_2H_5)_4OH$, or the ethyl representative of ammonium hydrate, NH_4OH. The solution of this tetrethylammonium hydrate is comparable with that of caustic potash in its basic power, but it does not redissolve chromic hydrate. Its platinum compound has the formula $[N(C_2H_5)_4]_2PtCl_6$.

The analogous methyl compounds are formed by similar methods. *Methylamine*, $(CH_3)H_2N$, is a colourless, easily combustible gas at ordinary temperatures, as we have already seen (p. 122). *Dimethylamine*, $(CH_3)_2HN$, is a colourless alkaline liquid below $9°$. Trimethylamine, $(CH_3)_3N$, is a colourless liquid below $10°$, which has a strong fishy odour. Salts of it are found in herring brine ; it is present in quantity in the products of distillation of the 'vinasses,' or mother liquor from which beetroot sugar has separated.[1] Tetramethylammonium iodide,

[1] Trimethylamine from this source is now used on a large scale in the manufacture of potassium carbonate directly from the chloride, just as ammonia is employed for sodium carbonate (see Part III., SODIUM). Trimethylamine must be used instead of ammonia, because its chloride is much more soluble than

$N(CH_3)_4I$, is obtained in the same way as the ethyl compound, and affords a corresponding tetramethyl-ammonium hydrate, $N(CH_3)_4OH$. The higher homologues of ethyl afford bases analogous to those of ethyl and methyl.

Again, amines can be obtained in which different alcohol radicals are present. Thus, by the action of ethyl iodide on methylamine, the *methylethylamine* can be ultimately separated, and the latter, when treated with propyl iodide, can afford *methylethylpropylamine*.

$$\left.\begin{array}{c} CH_3 \\ H \\ H \end{array}\right\} \quad : \quad \left.\begin{array}{c} CH_3 \\ C_2H_5 \\ H \end{array}\right\}N \quad : \quad \left.\begin{array}{c} CH_3 \\ C_2H_5 \\ C_3H_7 \end{array}\right\}N.$$
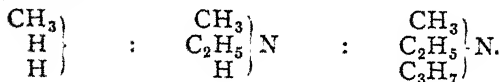
It is possible to go one stage further, and, by addition of butyl iodide to the last-named body, produce the *iodide of methylethylpropylbutylammonium*—a rather complex body with a cumbrous name.

It is evident that cases of metamerism must frequently occur among these ammonia derivatives : thus, dimethylamine and ethylamine are metamers, as are trimethylamine and propylamine, viz. :—

$$\left.\begin{array}{c} CH_3 \\ CH_3 \\ H \end{array}\right\}N \quad : \quad \left.\begin{array}{c} C_2H_5 \\ H \\ H \end{array}\right\}N \quad \text{and} \quad \left.\begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \end{array}\right\}N \quad : \quad \left.\begin{array}{c} C_3H_7 \\ H \\ H \end{array}\right\}N.$$
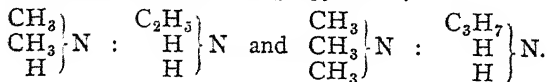
It is therefore necessary to have some means whereby primary, secondary, and tertiary amines can be distinguished.

One method is sufficiently obvious, and consists in

$KHCO_3$; whereas the latter and ammonium chloride have nearly the same solubility, and therefore cannot be separated.

heating the body in a pressure tube with excess of methyl iodide; an *ammonium* iodide is thus obtained and then analysed. If the amine treated were *tertiary* (*i.e.* already contained three alcohol radicals), we can simply add on to it methyl iodide; if *secondary* another methyl group will be introduced instead of hydrogen, and if *primary* two methyl groups will replace hydrogen.

Another method depends on the action of potassium *nitrite* when distilled with the solutions of the chlorides of the bases, or *alkylammonias* as they are often termed. The *tertiary* amine salt is not affected by the nitrite. The chloride of the *primary* probably becomes a nitrite, which latter, however, immediately breaks up into an alcohol, water, and nitrogen. Thus in the case of ethylammonium nitrite [1]—

$$\left.\begin{array}{c} C_2H_5 \\ H_3 \end{array}\right\} N-O-NO = C_2H_5OH + 2N + H_2O.$$
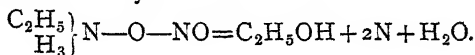
The *secondary* nitrite reacts in a wholly different manner. Thus diethylammonium nitrite affords the following products:—

$$\left.\begin{array}{c} C_2H_5 \\ C_2H_5 \\ H_2 \end{array}\right\} N-O-NO = \left.\begin{array}{c} C_2H_5 \\ C_2H \\ ON \end{array}\right\} N + H_2O.$$
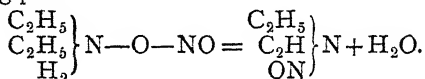
The new body is termed *diethylnitrosamine*; it is a yellow oil, lighter than water; it boils at 177°. Diethylammonium chloride is re-formed when the nitrosamine is heated with hydrochloric acid and water; nitric oxide gas is evolved at the same time.

If a salt of diethylamine can be obtained, the

[1] Ammonium nitrite under similar conditions affords nitrogen gas and water.

preparation of the nitrosamine from it is very easy and does not require distillation.

Experiment 717. — Make a small quantity of aqueous solution of diethylammonium chloride, and add to it a very strong *neutral* solution of potassium nitrite, made by passing N_2O_3 gas into caustic potash until the latter is saturated. On warming the mixture the nitrosamine rises to the surface as a yellow oil.

When the nitrosamine is treated with zinc and acetic acid, the oxygen of the NO group is replaced by hydrogen, and an ethylic compound of a new class of basic bodies termed *hydrazines* is formed, thus—

$$(C_2H_5)_2N—NO + 4H = (C_2H_5)_2N—NH_2 + H_2O.$$
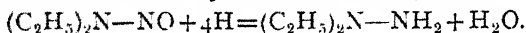
The new base is *diethylhydrazine*,[1] and is remarkable in that it may be regarded as an ethylated derivative of the *diamidogen* or *hydrazine* recently discovered by Curtius— $H_2N—NH_2$.

It is evident that the diethylhydrazine obtained from the nitrosamine is *unsymmetrical*, as both ethyl groups are, owing to the mode of generating the body, united to the same nitrogen atom. A metameric *symmetrical* diethylhydrazine is obviously possible.

Diethylhydrazine unites with a molecule of ethyl iodide and forms a crystalline compound whose formula may be written—

$$\left.\begin{array}{l} C_2H_5 \\ C_2H_5 \\ C_2H_5 \\ H_2N \end{array}\right\} NI.$$
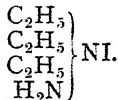
This is *triethylazonium iodide.*

[1] Monethyl hydrazine and its homologues are also known, but are formed in reactions of a different order.

IV.   K

If diethylhydrazine be *oxidised*, two molecules lose two atoms of hydrogen each, and the residues unite to form a powerful liquid base which is exceptionally rich in nitrogen, and is termed *tetrethyltetrazone*. The best oxidising agent is mercuric oxide which is reduced to mercurous oxide.

The essential change may be thus represented:—

$$\begin{matrix} (C_2H_5)_2N-NH_2 \\ (C_2H_5)_2N-NH_2 \end{matrix} + 2O = \begin{matrix} (C_2H_5)_2N-N \\ \| \\ (C_2H_5)_2N-N \end{matrix} + H_2O.$$
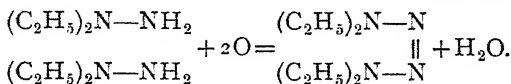
Analogous bodies can be obtained from dimethylhydrazine and from the higher homologues.

Ammonia, NH_3, *phosphine*, PH_3, *stibine*, SbH_3, and *arsine*, AsH_3, are similar hydrides, and the three latter resemble ammonia in affording ethylated, methylated, and other derivatives. Those derived from *phosphine* are ethyl-, diethyl-, and triethylphosphine—

$$\left. \begin{matrix} C_2H_5 \\ H \\ H \end{matrix} \right\} P : \left. \begin{matrix} C_2H_5 \\ C_2H_5 \\ H \end{matrix} \right\} P : \left. \begin{matrix} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{matrix} \right\} P.$$
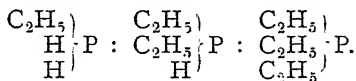
And the last can unite with ethyl iodide and afford *tetrethylphosphonium* iodide and hydrate—

$$\left. \begin{matrix} C_2H_5 \\ C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{matrix} \right\} PI : \left. \begin{matrix} C_2H_5 \\ C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{matrix} \right\} POH.$$
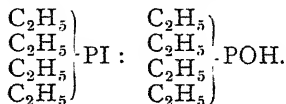
These bodies are obtained directly or indirectly from phosphonium iodide, H_4PI. Most are spontaneously inflammable liquids. Triethylphosphine possesses the remarkable property of uniting directly

with carbon bisulphide to form a fine red crystalline compound – $(C_2H_5)_3P.CS_2$.

Carbon bisulphide can be easily detected in coal gas by means of the phosphine.

Derived from *stibine*, SbH_3, the compounds $(C_2H_5)_3Sb$ and $(C_2H_5)_4SbI$ have been obtained ; but the mono- and diethylic derivatives are not yet known.

Derived from *arsine*, AsH_3, are the compounds $(C_2H_5)_3As$ and $(C_2H_5)_4AsI$; but mono- and diethylic arsines, in the strict sense of the terms, are not known. The tertiary compound is best obtained by the action of zinc ethide on arsenic trichloride—

$$3(C_2H_5)_2Zn + 2AsCl_3 = 2(C_2H_5)_3As + 3ZnCl_2.$$
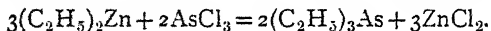
The methyl derivatives are obtained in the same way. The arsenic compounds like those of phosphorus easily oxidise, and in this respect are unlike the nitrogen derivatives while resembling the organo-metallic bodies.

Although arsenic does *not* afford a secondary or dimethyl arsine, an arsenic analogue of a *hydrazine* containing two methyl groups for each atom of arsenic is readily obtained.

Experiment 718.—Make a small quantity of an intimate mixture of arsenious oxide with about twice its weight of potassium acetate, and heat the dry mixture in a test-tube. A most offensive odour is developed.[1] As the product is highly poisonous, it

[1] This is an excellent test for arsenious oxide on the one hand, or an acetate on the other.

is not desirable to produce much of it; but when the distillation is conducted on a sufficient scale and under safe conditions, a liquid is condensed which sometimes ignites spontaneously. This, the *alkarsin*, or *fuming liquor of Cadet*, has been made the subject of a most elaborate research by Professor Bunsen, of Heidelberg, who found that the liquid chiefly consists of the compound $(CH_3)_4As_2O$, termed *cacodyl* [1] *oxide*, which boils at $150°$. This body results from the action of one molecule of arsenious oxide or four molecules of potassium acetate—

$$4(CH_3-CO-OK) + \begin{matrix} OAs \\ \\ OAs \end{matrix}\Big\rangle O =$$

$$\begin{matrix} (CH_3)_2As \\ \\ (CH_3)_2As \end{matrix}\Big\rangle O + 2CO(OK)_2 + 2CO_2$$
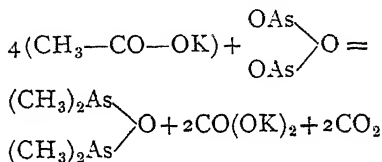
When cacodyl oxide is heated with zinc and hydrochloric acid in an atmosphere free from oxygen, the oxide is reduced to *cacodyl*.

$$\begin{matrix} (CH_3)_2As \\ \\ (CH_3)_2As \end{matrix}\Big\rangle O + 2H = \begin{matrix} (CH_3)_2As \\ | \\ (CH_3)_2As \end{matrix} + H_2O.$$
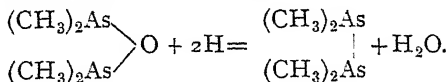
Cacodyl is a liquid which boils at $170°$ and ignites spontaneously in air. It is present in the crude oxide, and often communicates to the latter the property of igniting on contact with air.

When cacodyl is slowly acted on by air or oxygen, the oxide is partly reproduced. As already stated, the latter body is highly poisonous, but when the oxide is

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[1] κακώδης, stinking.

boiled with mercuric oxide and water an acid is obtained which contains more than 54 per cent. of arsenic, yet it is *not poisonous.* The acid in question is *cacodylic acid,* and it is formed in the following reaction :—

$$(CH_3)_2As\diagdown O + 2HgO + H_2O =$$
$$(CH_3)_2As\diagup$$
$$2\left((CH_3)_2As\diagup^O_{OH}\right) + 2Hg.$$
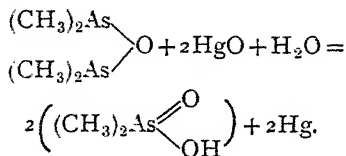
Cacodylic acid is a *saturated* compound which is not easily decomposed, and is an excellent example of the general principle that physiologically inert substances are often produced by the chemical saturation of previously active molecules.

Boron trimethide, $(CH_3)_3B$, and *triethide,* $(C_2H_5)_3B$, can be obtained by the action of zinc methide or ethide on boron trichloride.

Silicon tetramethide, $(CH_3)_4Si$, is formed when silicon tetrachloride is heated with zinc methide. The product boils at 30°. *Silicon tetrethide* is produced when zinc ethide acts on the tetrachloride of silicon ; it is a liquid which boils at 153°.

These silicon compounds are remarkable among substances of their class, because they act like hydrocarbides whose carbon has been partially replaced by the closely analogous element silicon, thus—

$$Si(CH_3)_4 \text{ acts like } C(CH_3)_4$$
$$Si(C_2H_5)_4 \quad ,, \quad C(C_2H_5)_4.$$
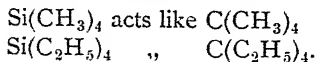
It was suggested in 1870 by Friedel and Crafts that silicon tetrethide should be regarded as the *hydride of silico-nonyl*, and might bear the same relation to a silico-nonyl alcohol as ethyl hydride does to ethyl alcohol. This idea was justified by the result, for on treating silicon tetrethide with chlorine the compound $SiC_8H_{19}Cl$ was obtained; this, on heating with silver acetate, gave $SiC_8H_{19}-O-C_2H_3O$, and the latter when carefully saponified afforded $SiC_8H_{19}-OH$, which boils at 190°, and is a well-defined silico-carbon alcohol. Other and similar alcohols have been obtained as well as acids, *e.g.* silico-propionic acid.

We have now completed our study of the more important derivatives of the paraffins and their related bodies. Before the student proceeds further it is desirable that he should draw up a table exhibiting the relations of the typical compounds dealt with in the preceding chapters. This will not only refresh the memory, but serve as a foundation for further study, as the space at our disposal obliges us to treat the remaining groups of organic compounds in much less detail than those of paraffin series.

CHAPTER LIV.

OLEFIANT GAS OR ETHYLENE—ITS HOMOLOGUES—
ETHYLENE CHLORIDE — BROMIDE — CYANIDE —
ACETATES — GLYCOL — DIATOMIC ALCOHOLS —
CHLORHYDRINE—ETHYLENE OXIDE—CONDENSED
GLYCOLS : HYDRATE AMINES, CHOLINE, NEURINE
—ISETHIONIC ACID—TAURINE—DIAMINES—MER-
CAPTANS.

WHEN ethyl alcohol is boiled with an excess of sul-
phuric acid, the latter removes the elements of water
from the alcohol, and colourless *olefiant gas* is evolved,
whose composition is represented by the symbol

$$C_2H_4.$$

The details of preparation, of composition, and the
chief properties of this body have been sufficiently
dealt with in Chapter XXI.; it is therefore unnecessary
to repeat them here. The higher alcohols of the
ethylic series afford homologues of olefiant gas by
dehydration. The names of these bodies are formed
by adding *ene* to that of the alcohol radical from
which each is derived : thus olefiant gas derived from
ethyl alcohol is *ethylene*. The following list includes
the chief members of the series known. Methylene,
CH_2, does not appear to be capable of existing in the
free state.

HYDROCARBIDES, C_nH_{2n}.

Ethylene	.	. C_2H_4	.	. Gas
Propylene	.	. C_3H_6	.	. ,,
Butylene	.	. C_4H_8	.	. ,,
Amylene	.	. C_5H_{10}	.	. b.-p. $39°$
Hexylene	.	. C_6H_{12}	.	. ,, $67°$
Heptylene	.	. C_7H_{14}	.	. ,, $95°$
Octylene	.	. C_8H_{16}	.	. ,, $125°$

Several of the higher members are met with in Burmese petroleum. Many isomers of these hydrocarbides are known.

When ethylene is shaken up with strong sulphuric containing a little of the anhydride in solution, the gas is absorbed and *sulphovinic acid* is formed—

$$C_2H_4 + H_2SO_4 = \genfrac{}{}{0pt}{}{C_2H_5}{H} \!\!\Big\rangle SO_4.$$
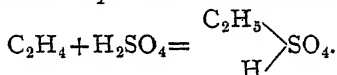
When the product is considerably diluted with water and distilled, *ethyl alcohol* is obtained.[1]

$$\genfrac{}{}{0pt}{}{C_2H_5}{H} \!\!\Big\rangle SO_4 + HOH = C_2H_5OH + H_2SO_4.$$
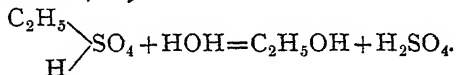
We can thus *pass back* from ethylene to the alcohol from which it was generated, and this method is general in application.

It has been proposed that alcohol should be

[1] The reader is advised to draw up a list of the various reactions in which ethyl alcohol and sulphuric acid are jointly concerned, in order that he may clearly understand the effect of varying conditions in determining the direction of chemical changes.

manufactured as above from coal gas, which contains 4 to 7 per cent. of ethylene, but the treatment has the disadvantage of depriving the gas of the constituent on which its illuminating power largely depends.

The *unsaturated* condition of ethylene has been already demonstrated. We found in the course of Experiment 257 that when olefiant gas is mixed with an equal volume of chlorine combination ensues, and the mixture loses its yellow colour, while *oily* drops collect on the sides of the vessel in which such a mixture is allowed to stand. To this *oil-making* property the compound owes its name of *olefiant gas.* The liquid formed, or 'Dutch liquid,' consists of

$$C_2H_4Cl_2, \text{ which boils at } 85°,$$

and is obviously a product of the direct addition of two atoms of chlorine to the olefiant gas molecule ; the latter, therefore, acts as an unsaturated *diad* group.

Dutch liquid is identical in composition and molecular weight with ethidene chloride, which is obtained when phosphorus pentachloride acts on aldehyde (see page 87), but the latter boils at 60° ; moreover, we have unmistakable evidence that its structure is represented by the following expression—

$$CH_3—CHCl_2.$$
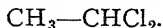
It is therefore an *unsymmetrical* chloride, since both chlorine atoms are attached to the same carbon. One *symmetrical* metamer of this—

$$ClH_2C—CH_2Cl,$$
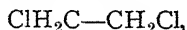
is obviously possible, and all the reactions of Dutch

liquid point it out as that body. We also infer that olefiant gas itself is a symmetrical hydride whose relation to its chloride may be thus shown :—

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \quad : \quad \begin{matrix} CH_2Cl \\ | \\ CH_2Cl. \end{matrix}$$
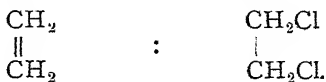
If the hydrocarbide be termed *ethylene*, Dutch liquid is *ethylene dichloride*.

Ethylene can not only afford *addition* products such as the dichloride, but a complete series of *substitution* compounds as well, by the continued action of chlorine.[1] The bodies so formed are metamers of those obtained by the chlorination of ethyl chloride, with the exception of the two end products, which are the same in both series. The following table includes the two groups of compounds :—

From ethylene.	From ethyl chloride.
$C_2H_4Cl_2$ b.-p. 82°	$C_2H_4Cl_2$ b.-p. 57°
$C_2H_3Cl_3$,, 115°	$C_2H_3Cl_3$,, 75°
$C_2H_2Cl_4$,, 137°	$C_2H_2Cl_4$,, 127°

$$C_2HCl_5 \text{ b.-p. } 158°$$
$$C_2Cl_6 \quad ,, \quad 182°.$$

Ethylene combines as readily with bromine as with chlorine, and the preparation of the bromide, $C_2H_4Br_2$,

---

[1] When $C_2H_4Cl_2$ is heated with caustic potash, HCl is removed and C_2H_3Cl, or *monochlorethylene*, is formed. The residual hydrogen of that body can also be successively replaced by chlorine, and then the following compounds are obtained : CH_2Cl_2, C_2HCl_3, and C_2Cl_4—the last is the so-called *bichloride of carbon* discovered by Faraday.

can be easily carried out, while the product is more useful than the chloride.

Experiment 719.—Bend a piece of glass tubing, rather wider than that used for gas delivery, into the zigzag form shown in Fig. 156, the object being to have a number of sharp bends ; the latter may be only a few centimeters apart. Pour some bromine into the tube through *a*, and manage to so distribute

Fig. 156.
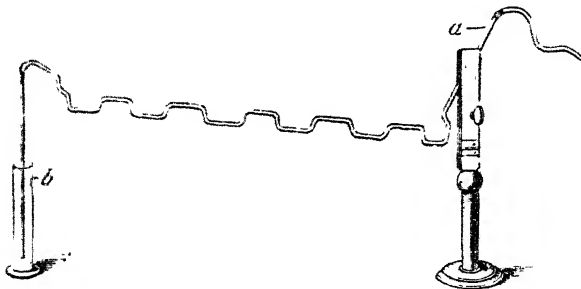
the bromine that there shall be a quantity at each of the bends when the tube is placed in the position shown. Now connect *a* with a gas-holder containing ethylene, and allow the gas to slowly bubble through the bromine. The liquid in the first bend slowly loses its colour, and ultimately becomes quite colourless, and if the current of gas be maintained the bromine at successive bends undergoes complete conversion into ethylene dibromide. The jar *b* should contain some lime to absorb bromine vapours. The product is poured out into a cylinder, and washed with water containing a little sodium carbonate, in

which it is scarcely soluble ; it is then drawn off, dried with calcium chloride, and distilled.

Pure *ethylene dibromide* is a colourless liquid of 2·16 specific gravity : it boils at 131°. It readily mixes with alcohol and ether, but not with water.

A corresponding chlorobromide was obtained by Simpson by passing ethylene into solution of chloride of bromine in water. The corresponding iodide and chloriodide are also known.

Ethylene dicyanide was obtained by Maxwell Simpson on heating ethylene dibromide with potassium cyanide in alcohol.

$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + 2KCN = \begin{matrix} CH_2—CN \\ | \\ CH_2—CN \end{matrix} + 2KBr.$$
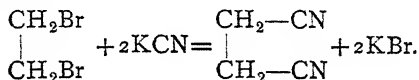
Potassium bromide separates, and the dicyanide or *succinonitrile* can be obtained on evaporation. It is a solid which fuses at 55° (see *Succinic acid*).

It is evident that ethylene dibromide, if analogous to ethyl bromide, should be able to exchange its bromine for oxidised radicals. When the dibromide is heated in a tube with silver acetate and acetic acid, the following change takes place :—

$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + 2AgO—C_2H_3O = \begin{matrix} CH_2O—C_2H_3O \\ | \\ CH_2O—C_2H_3O \end{matrix} + 2AgBr.$$

Ethylene
dibromide

Ethylene
diacetate
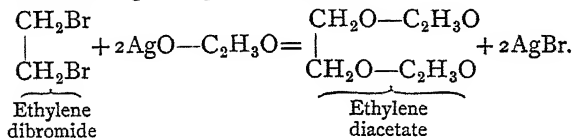
The diacetate $C_2H_4(O—C_2H_3O)_2$ is obviously analogous to the acetate of a *diad metal* such as calcium, $Ca(O—C_2H_3O)_2$, just as ethyl acetate,

$\overset{..}{C}_2H_5O—C_2H_3O$, is analogous to the salt of a *monad metal* like potassium, *e.g.* the acetate $KO—C_2H_3O$.

Another ethylene acetate may be very easily produced from the bromide without the use of the silver salt.

Experiment 720.—Pour into a stout bottle of about 200 c.cs. capacity 10 grams of ethylene dibromide, add 10 grams of anhydrous potassium acetate in powder, and 30 c.cs. of nearly absolute alcohol. Tie down the cork of the bottle securely, and place in a water-bath, whose temperature is gradually raised to boiling. Continue to heat for about two hours, then allow to cool down. The liquid in the bottle is filtered from a quantity of potassium bromide which has separated, and is then distilled : ethyl acetate and unchanged alcohol pass over first ; the temperature quickly rises to 130°, and all liquid coming over at or above that point should be collected apart. By further fractionation a liquid can be separated which is *ethylene hydrate acetate*—

$$CH_2—OH$$
$$CH_2—OC_2H_3O.$$
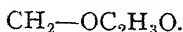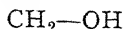
This compound boils at 182° ; it easily mixes with water. The formation of this body from the dibromide is thus explained :—

$$\begin{matrix} CH_2—Br \\ | \\ CH_2—Br \end{matrix} + 2KOC_2H_3O + C_2H_5OH =$$

$$\begin{matrix} CH_2—OH \\ | \\ CH_2—OC_2H_3O \end{matrix} + 2KBr + C_2H_5OC_2H_3O.$$
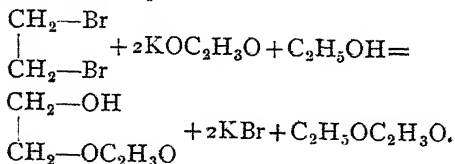
It is evident that this body is half ester and half *alcohol* ; and it should be possible to replace the acid radical by another hydroxyl group and so obtain *ethylene dihydrate* or *ethylene alcohol.* Such a change readily takes place when the warm hydrate acetate is shaken up with a hot and strong solution of caustic potash until the mixture remains persistently alkaline. Saponification is effected thus :—

$$\begin{array}{c} CH_2-OH \\ | \\ CH_2-OC_2H_3O \end{array} + KOH = \begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array} + KOC_2H_3O.$$
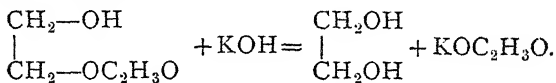
The liquid is then saturated with carbon dioxide gas to remove free alkali, and distilled. Water passes over first, and then a liquid which, when pure, boils at 197°. This is the dihydroxy or diatomic alcohol in question : it is a syrupy liquid of sp. gr. 1·125, easily miscible with water and ethyl alcohol, but not with ether. It has a sweet taste and has in consequence been named *glycol* by Wurtz, its discoverer.

This body is a type of a series of diatomic alcohols obtainable by similar methods from the higher homologues of ethylene. All these bodies are called *glycols.*[1] Numerous isomers are met with among the higher terms, and some of these must be referred to later on ; but no metameric *dicarbon* glycol is known. In diethyl acetal, $CH_3-CH(OC_2H_5)_2$, we have a representative of a possible metamer, $CH_3-CH(OH)_2$, or ethidene alcohol, but (as already pointed out at page 91) a single carbon atom very seldom forms a stable compound with two hydroxyl groups directly, so that if dihydroxy

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[1] For condensed glycols, see page 146.

ethidene alcohol exists it is probably as unstable as carbonic acid, $CO(OH)_2$.

Glycol can afford two classes of esters by successive replacement of hydroxyl hydrogen by acid radicals. The diacid esters, of which the diacetate and dichloride may be taken as types—

$$CH_2-OC_2H_3O \qquad CH_2Cl$$
$$\qquad\qquad\qquad : $$
$$CH_2-OC_2H_3O \qquad CH_2Cl,$$
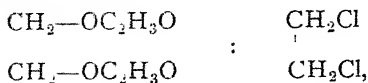
are seldom completely formed by the direct action of the acid on the glycol ; they are most readily produced, as in the case of the diacetate, by the action of the bromide or chloride on the silver salt of the acid radical ; in the cases of the homologous compounds, they are formed either by the direct union of chlorine, bromine, &c., with the hydrocarbide, or by the action of phosphorus pentachloride, bromide, &c., on the glycol.

The case is different with the monacid esters. These bodies, *which are half alcohol, half ester*, are readily obtained by the direct action of the acid on the glycol. In this way the typical compounds—

$$CH_2-OH \qquad\qquad CH_2-OH$$
$$\qquad\qquad and $$
$$CH_2-OC_2H_3O \qquad\quad CH_2-Cl$$
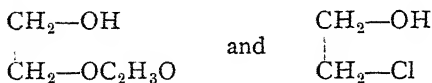
can be produced. We shall now prepare a little of the chlorhydrate.

Experiment 721.—Pass dry hydrochloric acid gas into a small quantity of glycol contained in a well-cooled test-tube ; the gas is absorbed, and when the liquid ceases to dissolve more it is gently heated to

expel excess, when a residue is obtained of the neutral chlorhydrate, or *chlorhydrine,* as the body is commonly termed.

$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} + HCl = \begin{array}{l} CH_2-OH \\ | \\ CH_2-Cl \end{array} + H_2O.$$
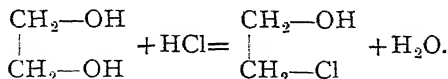
The chlorhydrine is a colourless liquid of sp. gr. 1·24, which boils at 131°.

The same compound can be directly formed from ethylene by the action of hypochlorous—

$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + ClOH = \begin{array}{l} CH_2-OH \\ | \\ CH_2-Cl \end{array}$$
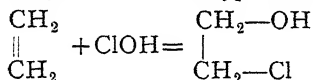
and by the action of chloride of sulphur on glycol.

When acted on by nascent hydrogen, the chlorhydrine affords ethyl alcohol—

$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-Cl \end{array} + 2H = \begin{array}{l} CH_2-OH \\ | \\ CH_3. \end{array}$$
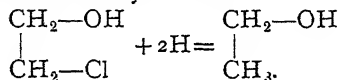
These facts confirm the conclusion already drawn from other evidence of the structure of glycol[1] and its relations to ethyl alcohol.

When the chlorhydrine is heated with potassium cyanide, *ethylene cyanhydrine* is obtained—

$$\begin{array}{l} CH_2OH \\ | \\ CH_2Cl \end{array} + KCN = \begin{array}{l} CH_2OH \\ | \\ CH_2CN \end{array} + KCl.$$
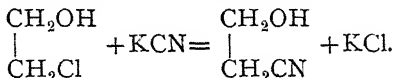
This body is metameric with Simpson's ethidene cyanhydrine from aldehyde, and is the nitrile of a lactic acid (see page 161).

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[1] Like ethyl alcohol the hydroxyl hydrogen of glycol can be replaced by sodium, but in two stages forming mono- and di-sodium ethylenates.

It is evident that ethylene glycol should afford an oxide bearing the same relation to glycol that ethyl oxide does to ethyl alcohol. Direct dehydration of glycol fails to produce free ethylene oxide ; but that body can be easily obtained from the chlorhydrine.

Experiment 722.—Add to the chlorhydrine prepared in the last experiment some strong caustic potash, and warm the mixture. A colourless gas is soon given off which can be inflamed at the mouth of the tube. The gas evolved is *ethylene oxide*, resulting from the abstraction of HCl from the chlorhydrine —

$$\begin{matrix} CH_2\text{—}OH \\ | \\ CH_2\text{—}Cl \end{matrix} + KOH = \begin{matrix} CH_2 \\ \diagdown \\ CH_2 \diagup \end{matrix} O + KCl + H_2O.$$
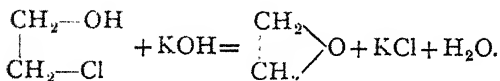
The oxide is a gas at ordinary temperatures, but can be readily condensed by cold to a neutral liquid which boils at 13° ; it is easily soluble in water and alcohol. When its aqueous solution is warmed with ammonia-silver nitrate, it does *not* reduce silver, and is thus easily distinguished from ordinary aldehyde with which it is metameric ; moreover, it does *not* combine with acid sulphites.

It rapidly unites with hydrochloric acid and reproduces the chlorhydrine ; in this respect it exhibits marked basic properties. This is further shown by its precipitation of magnesium hydrate when the gaseous oxide is passed into a warm solution of magnesium chloride.

Ethylene oxide slowly combines with water and forms glycol ; but it also combines with the alcohol

IV.   L

and affords *condensed glycols.*   Heated with one mole‡
cule of glycol we obtain

$$HO—C_2H_4—O—C_2H_4—OH.$$
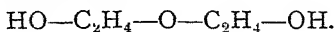
With two molecules of oxide to one of glycol there
results

$$HO—C_2H_4—O—C_2H_4—O—C_2H_4—OH.$$
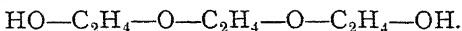
With a larger excess of oxide,

$$HO—C_2H_4—O—C_2H_4—O—C_2H_4—O—C_2H_4—OH,$$
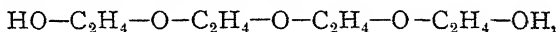
and so on.

Ethylene oxide unites directly with ammonia and
amines, but the bodies which it forms with them are
not analogous to those afforded by aldehydes.   With
ammonia it produces a compound which is half amine
and half alcohol, termed a *hydrate amine*; this is basic.

$$HO—CH_2—CH_2—NH_2.$$
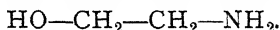
Ethylene-hydrate ammonium chloride—
$$HO—CH_2—CH_2—NH_3Cl,$$
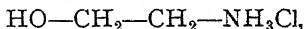
is formed by the action of ammonia on ethylene
chlorhydrine. If, however, we act on the chlorhydrine
with trimethylamine instead of ammonia, the com-
pound—

$$HO—CH_2—CH_2—N(CH_3)_3Cl$$

is produced, which latter affords the hydrate—

$$HO—CH_2—CH_2—N(CH_3)_3OH$$
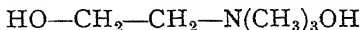
when treated with silver hydrate (*i.e.* silver oxide and
water).   The compound so formed is identical with a
complex basic body termed *choline*, which can be sepa-
rated from human bile, from nerve and brain sub-

stance, and has lately been extracted from *hops*. By the loss of the elements of water choline can afford *neurine*, which also occurs in nerve or brain tissue. This remarkable synthesis of chlorine was effected by Liebreich.

Another important synthesis which begins with ethylene chlorhydrine is that of *taurine*—an important constituent of bile which contains sulphur.

The first step in this synthesis consists in the formation of the ethylene-hydrate sulphonic acid (isethionic acid [1]), or rather of its potassium salt, by the action of the chlorhydrine on potassium sulphite—

$$HO—C_2H_4—Cl + KSO_3K =$$
$$HO—C_2H_4—SO_3K + KCl.$$
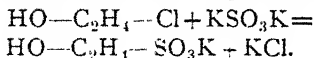
The sulphonate, treated with phosphorus penta-chloride, affords the product

$$Cl—C_2H_4—SO_2Cl,$$

which becomes

$$Cl—C_2H_4—SO_2OH$$
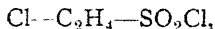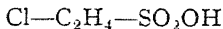
when acted on by water. The chlorethylene sulphonic acid, when heated with ammonia, affords

$$NH_2—C_2H_4—SO_2OH,$$
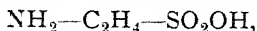
or *amid-ethylene-sulphonic acid* (amidisethionic acid), which is identical with *taurine* obtained from bile.

Just as the group $HO—C_2H_4$ acting as a monad can replace hydrogen in ammonia and produce ethylene-hydrate-amine, so can successive atoms of hydro-

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[1] Also obtained by the action of sulphur trioxide on absolute alcohol—

$$C_2H_5OH + SO_3 = HO—C_2H_4—SO_4H.$$
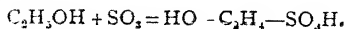
gen be similarly substituted in ammonia, and the following series be obtained :—

$$\text{Primary . . . } HO—C_2H_4'—NH_2$$
$$\text{Secondary . } (HO—C_2H_4)'_2=NH$$
$$\text{Tertiary . . } (HO—C_2H_4)'_3\equiv N.$$
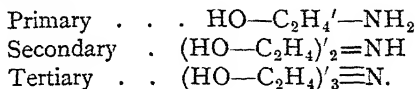
But these bodies evidently form a class apart from such ammonia derivatives as mono-, di-, and tri-ethylamine. Ethylene analogues of the latter exist, however, and are easily formed by the action of ethylene bromide on alcoholic ammonia.

Experiment 723.—Gently heat a mixture of ethylene bromide and solution of dry ammonia gas in alcohol, in a sealed tube, for two hours ; then open the tube and distil off the liquid, when a solid crystalline residue is obtained, consisting of the bromides of several ethylene ammoniums. The residue distilled with caustic potash affords the amines—

Primary.		Secondary.		Tertiary.
$\left.\begin{array}{l}C_2H_4\\ \ \ H_2\\ \ \ H_2\end{array}\right\}N_2$	:	$\left.\begin{array}{l}C_2H_4\\ C_2H_4\\ \ \ H_2\end{array}\right\}N_2$	:	$\left.\begin{array}{l}C_2H_4\\ C_2H_4\\ C_2H_4\end{array}\right\}N_2.$
B.-p. 124°.		B.-p. 170°.		B.-p. 210°.
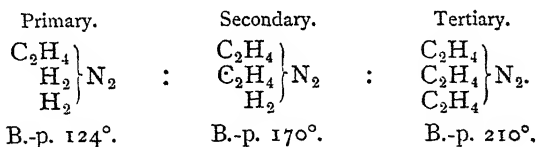
These are powerful bases, and are formed on the type of the *double* molecule of ammonia ; they are termed *diamines*. Each diamine can unite with *two* molecules of hydrobromic or other monobasic acid, and form the corresponding bromide of an ethylene-diammonium, *e.g.*—

$$(C_2H_4)_3N_2 + 2HBr = (C_2H_4)_3H_2N_2Br_2.$$
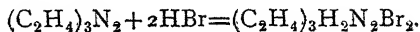
Triethylene diamine unites with one molecule of ethylene bromide, and forms

$$(C_2H_4)_4N_2Br_2,$$
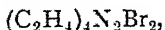
from which a corresponding hydrate can be obtained, as in the analogous cases of tetrethylammonium compounds.

Ethylene diamine very readily unites with the elements of water, and affords the compound

$$\begin{matrix} CH_2-NH_3 \\ \end{matrix}\!\!>\!\!O.$$
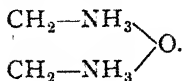
As a matter of fact, this is obtained when the primary bromide is distilled with potash; the water can only be completely eliminated by the action of sodium.

The primary diamines, when treated with nitrous acid, afford the *oxide* of the radical, nitrogen and water, instead of the *hydrate* or alcohol, as in the cases of the primary monamines.

Phosphorus, arsenic, and metallic compounds of ethylene and some of its homologues are known, but they are not of sufficient general importance to be specially described in this work.

The *sulphur glycol* or *mercaptan* is formed when ethylene bromide acts on potassium sulphydrate—

$$\begin{matrix} CH_2-Br \\ | \\ CH_2-Br \end{matrix} + 2KSH = \begin{matrix} CH_2-SH \\ | \\ CH_2-SH \end{matrix} + 2KBr.$$
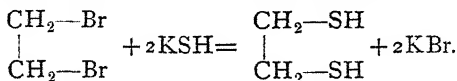
It is a colourless liquid, which boils at 146°.

When potassium sulphydrate is acted on by the chlor-
hydrine, a *hemi-mercaptan* is found—

$$\begin{matrix} CH_2—OH \\ | \\ CH_2—Cl \end{matrix} + KSH = \begin{matrix} CH_2—OH \\ | \\ CH_2—SH \end{matrix} + KCl.$$
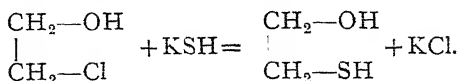
This body, when oxidised by nitric acid, affords
ethylene hydrate sulphonic acid or *isethionic acid*,
which can then be used to effect the synthesis of
taurine (*q.v.*)—

$$\begin{matrix} CH_2—OH \\ | \\ CH_2—SH \end{matrix} + 3O = \begin{matrix} CH_2OH \\ | \\ CH_2—SO_2OH. \end{matrix}$$
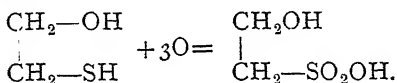
The sulphur analogue of the oxide, C_2H_4S, is also
known.

CHAPTER LV.

WHEN the monatomic alcohols are oxidised, they each afford in succession an aldehyde and an acid. The diatomic alcohols should give at least *two* acids, and possibly two aldehydes on similar treatment. We have, therefore, now to examine the products of oxidation of ethylene glycol. and, later on, some of those derivable from its homologues.

Experiment 724.—Moisten some platinum black with glycol, and expose in contact with litmus paper, as in Experiment 692. Acid is soon produced on exposure to the air, and the paper is easily reddened. The acid obtained in this way by limited oxidation of glycol is termed *glycolic acid*, $C_2H_4O_3$, and is found to be *monobasic*. It differs from acetic acid, $C_2H_4O_2$, in containing one atom of oxygen more, and is therefore often termed *oxyacetic acid*. Since it is monobasic it must contain one COOH group ; hence its

relation to glycol and acetic acid can be represented in the following way :—

$$
\begin{array}{ccccc}
\text{CH}_2\text{—OH} & & \text{COOH} & & \text{COOH} \\
| & : & | & : & | \\
\text{CH}_2\text{—OH} & & \text{CH}_2\text{OH} & & \text{CH}_3 \\
\underbrace{\qquad\qquad} & & \underbrace{\qquad\qquad} & & \underbrace{\qquad\qquad} \\
\text{Glycol.} & & \text{Glycolic acid.} & & \text{Acetic acid.}
\end{array}
$$
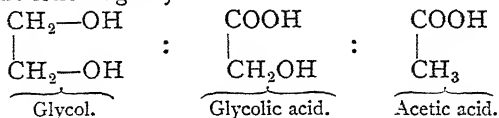
On this view it is half acid, half alcohol. More-over, it appears to be simply related to acetic acid, hydroxyl replacing one hydrogen atom in the methyl group. This view of its constitution is confirmed by the easy conversion of monochloracetic acid into glycolic acid by the action of boiling caustic potash.

Experiment 725.—Dissolve 3 or 4 grams of monochloracetic acid in about 20 c.cs. of water in a flask, and neutralise with caustic potash solution; note the volume of alkaline solution required for this purpose, and then add as much more, in other words *double* the volume required to neutralise. Now boil the mixture until it is reduced to a small bulk, allow to cool, then just neutralise any excess of alkali by dilute nitric acid, add neutral solution of copper nitrate, and let the mixture stand. A bluish com-pound slowly separates, which is *copper glycolate*, $Cu(C_2H_3O_3)_2$. When the solution of the copper salt in boiling water is treated with sulphuretted hydrogen in excess, the copper is precipitated as sulphide, and glycolic acid remains in solution, and can be obtained in crystals by careful evaporation. This conversion of chloracetic into glycolic acid [1] may be thus repre-sented :—

---

[1] If potassium *sulphydrate* be made to act on chloracetic acid, *thio-glycolic acid*, which is a hemi-mercaptan, is formed,

$$\begin{array}{c} COOH \\ | \\ CH_2Cl \end{array} + KOH = \begin{array}{c} COOH \\ | \\ CH_2OH \end{array} + KCl.$$
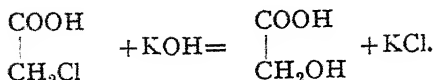
Glycolic acid melts at 80°. It is most easily precipitated as copper salt, which requires 130 parts of water at 10° for solution ; the calcium salt requires 75 parts of water to dissolve it. The acid is found in the leaves of the Virginian creeper and in unripe grapes, but is not present in the ripe fruit.

Glycolic acid yields an anhydride termed *glycolide* by simple heating until water is eliminated—

$$\begin{array}{c} CH_2OH \\ | \\ COOH \end{array} = \begin{array}{c} CH_2 \\ | \\ CO \end{array} \Big\rangle O + H_2O.$$
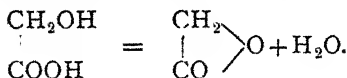
Glycolide is a powder which fuses at 220°. It is insoluble in water, but slowly combines with it and forms glycolic acid, which then dissolves.

When chloracetic acid is treated in alcoholic solution with sodium *methylate* or *ethylate* instead of hydrate, the OCH_3 or OC_2H_5 replace chlorine, and the following bodies are obtained :—

$$\begin{array}{c} COOH \\ | \\ CH_2OCH_3 \end{array} \quad : \quad \begin{array}{c} COOH \\ | \\ CH_2—OC_2H_5 \end{array}$$

Methyl glycolic acid.   Ethyl glycolic acid.
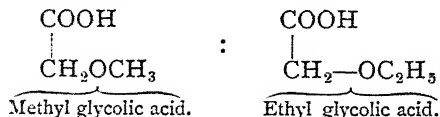
It is to be particularly noted that the carboxyl

$HS—CH_2—COOH$. When the sulphide of methyl is made to act on bromacetic acid, combination takes place, and the remarkable compound $Br(CH_3)_2S—CH_2—COOH$ is formed, which has been named *bromide of dimethylthetine* by Crum-Brown and Letts.

hydrogen of glycolic acids can alone be replaced by the *metal* of an alkaline hydrate.

It is evident that the second CH_2—OH group of glycol should be capable of oxidation into COOH, like the first.

We shall now effect this further oxidation of glycol.

Experiment 726.—Add some nitric acid to an aqueous solution containing some glycol or glycolic acid, and warm in a test-tube; ruddy fumes are evolved, indicating oxidation. When the chief action is over, boil for a short time, and evaporate a few drops of the liquid on a watch-glass; colourless crystals separate, which consist of *oxalic acid.* The latter can be recognised in the rest of the solution in the following way :—Add a few drops of calcium chloride solution, and then excess of ammonium hydrate; a white precipitate of *calcium oxalate,* CaC_2O_4,[1] is obtained, which is insoluble in free acetic acid, though easily dissolved by hydrochloric acid. The composition of calcium oxalate proves the acid to be *dibasic* : the relation of oxalic acid to glycol and glycolic acid is, therefore, the following :—

$$
\begin{array}{ccccc}
CH_2\!-\!OH & & COOH & & COOH \\
| & : & | & : & | \\
CH_2\!-\!OH & & CH_2\!-\!OH & & COOH \\
\underbrace{\qquad\qquad} & & \underbrace{\qquad\qquad} & & \underbrace{\qquad\qquad} \\
\text{Glycol.} & & \text{Glycolic acid.} & & \text{Oxalic acid.}
\end{array}
$$
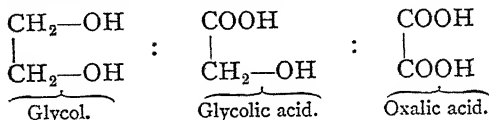
[1] The oxalate, when dry and heated on platinum foil, affords $CaCO_3$ and CO; and the residue, when raised to a still higher temperature, breaks up into CaO and CO_2.

The synthesis of oxalic acid from *cyanogen* has been effected by the action of water on the latter—

$$\begin{matrix} \text{CN} \\ | \\ \text{CN} \end{matrix} + 4H_2O = \begin{matrix} \text{COOH} \\ | \\ \text{COOH} \end{matrix} + 2NH_3.$$
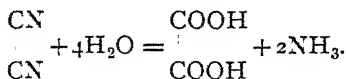
This change is analogous to the conversion of hydrocyanic acid (*formonitrile*) into formic acid (see p. 80), or of methyl cyanide (*acetonitrile*) into acetic acid (see p. 68); in the present case the *two* CN groups are changed to carboxyl. Cyanogen is, therefore, *oxalonitrile*.

Oxalic acid is a usual product of the prolonged oxidation of carbon compounds; thus, when starch or sugar is boiled for a considerable time with nitric acid, crystals of oxalic acid are obtained on evaporation. Again, when a mixture of sawdust with potassium and sodium hydrates is heated to a temperature short of charring, water extracts alkaline oxalate from the mass; the salt is then converted into calcium oxalate and caustic alkali by boiling with milk of lime. The alkali is used in a fresh operation, while the oxalate is treated with sulphuric acid, which sets free oxalic acid, and the latter can be crystallised out. This process, which is due to Dale, of Manchester, now enables the acid to be very cheaply produced.

Crystallised *oxalic acid*, $C_2O_4H_2, 2H_2O$, contains two molecules of water of crystallisation, which it parts with at 110°, while the true acid can be sublimed with some decomposition at 168°. Oxalic anhydride is unknown. We already know, from Experiment 249, that oxalic acid easily splits up into

carbon dioxide and monoxide when heated with sulphuric acid ; but if an oxidising body, such as potassium bichromate or permanganate, is present at the same time, oxidation occurs, and carbon dioxide alone is formed. The converse operation—*i.e.* the production of oxalic acid from carbon dioxide—has been effected by heating sodium mixed with sand to 360° in an atmosphere of carbon dioxide ; sodium oxalate, $C_2O_4Na_2$, results.

Oxalic acid, in the form of hydrogen potassium oxalate, C_2O_4KH, occurs in sorrel, *Oxalis acetosella*, and in rhubarb. The substance commonly sold as *salt of sorrel* is a compound of acid potassium oxalate with oxalic acid, $C_2O_4KH, C_2O_4H_2 2H_2O$. This is sometimes called 'quadroxalate of potassium.' Calcium oxalate, C_2O_4Ca, is formed as already described, and is the most characteristic salt of the acid ; it is met with in octahedral crystals in many plant tissues, and as a morbid product in urine. 'Mulberry calculus' consists of this body, and is easily recognised by its form and easy conversion into calcium carbonate when heated on platinum foil ; the residue then effervesces on addition of an acid.

We shall now describe a method by which glycolic and oxalic acids, with some related bodies of considerable interest, can be obtained directly from *ethyl* alcohol, when the latter is oxidised in a peculiar manner by nitric acid.

Experiment 727.—Obtain a tall jar, about 5 or 6 centimeters in diameter, capable of holding more than half a liter. Provide a thistle funnel whose tube can reach to the bottom of the jar ; let the end be

drawn out, so that the orifice may be small ; place it in the cylinder as shown (fig. 157). Now pour in 150 c.cs. of strong spirit of wine, and add, through the funnel, 70 or 80 c.cs. of water ; the latter must be poured in steadily, so that it may form a distinct layer below the lighter alcohol. Add, in the same way and very carefully, 80 c.cs. of yellow nitric acid of sp. gr. 1·4 to 1·45. If the acid were allowed to come in contact at once with the alcohol, *very violent action* would ensue, but if the operation is properly conducted the three liquids lie in the cylinder without mixing and in the order of specific gravity, the heavy nitric acid being below, and separated by a ' pad ' of water from the lighter alcohol, so that mixture can only take place by slow diffusion. Leave the cylinder in any outbuilding where it will not be disturbed. On standing, the acid slowly diffuses up and effects the gradual oxidation of the alcohol ; the acid becomes blue, owing to partial reduction to nitrous acid, and the odour of aldehyde is developed. The process is generally complete in a week or ten days, if the temperature be about 18°. Should complete diffusion not have taken place in the time, siphon off the liquid from any remaining acid.

FIG. 157.

The solution so obtained is found to contain the following bodies, which can be separated by means to be presently described :—

Glycolic acid, doubtless produced from glycol,

formed at an early stage of oxidation of ethyl alcohol—

$$CH_2OH \qquad \qquad CH_2—OH \qquad \qquad COOH$$
$$\qquad : \qquad \qquad : \qquad$$
$$CH_3 \qquad \qquad CH_2—OH \qquad \qquad CH_2OH$$

Ethyl alcohol.   Glycol.   Glycolic acid.
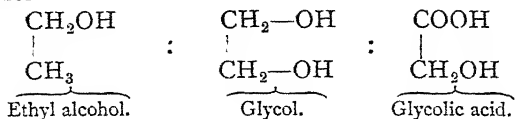
Glyoxalic (glyoxylic) acid, a body which results from the removal of two atoms of hydrogen from glycolic acid—

$$COOH$$
$$COH.$$

This body is half acid, half *aldehyde*, in its reactions.

Glyoxal, which is the *double aldehyde* of oxalic acid—

$$COH \qquad \qquad COOH$$
$$\qquad : \qquad$$
$$COH \qquad \qquad COOH$$

Glyoxal.   Oxalic acid.
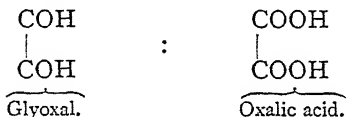
is present in the liquid and *oxalic acid*.

In order to separate these bodies, slowly evaporate the liquid in small separate quantities on ordinary plates until reduced to syrup; then dilute the residue with about ten volumes of water; add powdered chalk until effervescence no longer takes place on further addition; boil the liquid for some time and allow it to cool. Then add an equal volume of alcohol, mix, and stand. Filter the alcoholic solution, and press the precipitated calcium salts. The filtrate, when evaporated, leaves *glyoxal* as a syrupy liquid.

Like other aldehydes, glyoxal reduces ammonia-silver nitrate, and combines with acid sulphites of the alkali metals.

The mixture of calcium salts is boiled up with a considerable volume of water, and the liquid is filtered while hot. Calcium *oxalate* is left behind, as it is quite insoluble. The filtrate, when cool, deposits crystals of calcium *glyoxalate*, and this can be purified by another crystallisation from boiling water. Free glyoxalic acid can be obtained from the calcium salt by careful treatment with diluted sulphuric acid.

Most of the glycolate remains in solution with some glyoxalate; the latter is decomposed by boiling with calcium hydrate; any excess of the latter is removed by a current of carbon dioxide, and the filtered liquid allowed to stand, when calcium *glycolate* separates and can be collected. The mother liquor, when treated with copper nitrate, gives a precipitate of *copper glycolate.*

Aldehydic bodies, as well as acids, are thus recognisable among the products of oxidation of glycol.

The higher homologues of ethylene glycol can, like it, afford at least two acids on oxidation, one of these being homologous with glycolic and the other with oxalic acid.[1] It is desirable to repeat the remark here that the members of the glycolic series, although monobasic, can have the hydrogen of the alcoholic hydroxyl replaced by methyl, ethyl, &c., though not by metals; the latter only replace the carboxyl hydrogen under ordinary conditions. The following list includes the most important of these bodies :—

---

[1] Numerous isomers are known in both series.

GLYCOLS AND ACIDS.

Glycols.	Monobasic acids.	Dibasic acids.
$C_2H_4(OH)_2$	$CH_2(OH)COOH$ (Glycolic, or Oxyacetic)	$(COOH)_2$ (Oxalic)
$C_3H_6(OH)_2$	$C_2H_4(OH)COOH$ (Oxypropionic, or Lactic)	$CH_2(COOH)_2$ (Malonic)
$C_4H_8(OH)_2$	$C_3H_6(OH)COOH$ (Oxybutyric)	$C_2H_4(COOH)_2$ (Succinic)
$C_5H_{10}(OH)_2$	$C_4H_8(OH)COOH$ (Oxyvaleric)	$C_3H_6(COOH)_2$ (Glutaric)
$C_6H_{12}(OH)_2$	$C_5H_{10}(OH)COOH$ (Oxycaproic, or Leucic)	$C_4H_8(COOH)_2$ (Adipic)
$C_7H_{14}(OH)_2$	$C_6H_{12}(OH)COOH$ (Oxyheptylic)	$C_5H_{10}(COOH)_2$ (Pimelic)
$C_8H_{16}(OH)_2$	$C_7H_{14}(OH)COOH$ (Oxycaprylic)	$C_6H_{12}(COOH)_2$ (Suberic)
$C_nH_{2n}(OH)_2$	$C_nH_{2n}(OH)COOH$	$C_nH_{2n}(COOH)_2$

Having examined the typical acid at the head of each list in sufficient detail, we must now deal more generally with the higher members of the homologous series; in doing so it will be convenient to notice the chief *monobasic* acids of the glycolic or *lactic* group first.

MONOBASIC ACIDS.

General formula, $C_nH_{2n}(OH)COOH$.

Glycolic acid, $CH_2(OH)COOH$, already examined.

Lactic acids, $C_2H_4(OH)COOH$. Two metameric lactic acids are known which are different in chemical structure; one of these is derived from the normal propylene glycol, the other from isopropylene glycol and other sources; a third acid, which is identical with the last in chemical structure, but is distinguished chiefly by its power of rotating to the right a ray of polarised light passed through its solution, is met with in the juice of flesh, and is termed *sarcolactic acid*. This is a *physical isomer* (see page 183).

Normal lactic, oxypropionic, or *hydracrylic acid* is obtained by the oxidation of normal propylene glycol—

$$
\begin{array}{ccc}
CH_2\text{—}OH & & CH_2\text{—}OH \\
| & & | \\
CH_2 & \text{to} & CH_2 \\
| & & | \\
CH_2\text{—}OH & & COOH.
\end{array}
$$
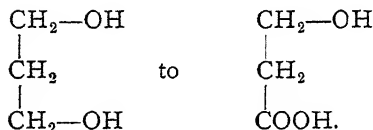
Or by the action of silver oxide and water on the chloro-, or the β-iodopropionic acid (*i.e.* from primary propyl alcohol), just as chloracetic acid gives glycolic acid. The relations of these bodies are evident from the formulæ—

$$
\begin{array}{ccccc}
CH_3 & & CH_2I & & CH_2OH \\
| & & | & & | \\
CH_2 & : & CH_2 & : & CH_2 \\
| & & | & & | \\
CH_2OH & & COOH & & COOH
\end{array}
$$

Normal Propyl alcohol.	β-Iodopropionic acid.	Oxypropionic acid.
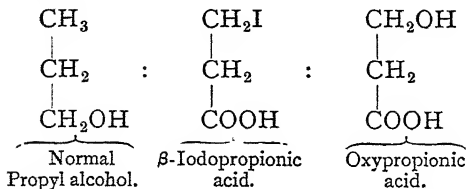
It is also formed when *ethylene cyanhydrin* (see page 144) is heated with hydrochloric acid.

This body is usually termed *hydracrylic* acid, because it easily decomposes into water and *acrylic acid*, $CH_2=CH—COOH$, which latter belongs to another series (see page 237).

Lactic acid, properly so called, because chiefly derived from fermented *milk*, is identical with the product of oxidation by isopropylene glycol—

$$
\begin{array}{ccc}
CH_3 & & CH_3 \\
| & & | \\
CH—OH & : & CH—OH \\
| & & | \\
CH_2—OH & & COOH.
\end{array}
$$
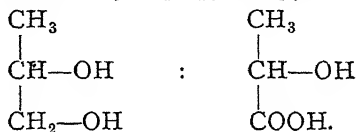
But it is most easily obtained in the following way from sour milk.

Experiment 728.—Take a liter of sour milk, add to it at least 100 grams of milk-sugar, then 200 grams of chalk, and some pieces of rotten cheese broken in fragments. The mixture should be allowed to stand in a warm place, so that the temperature may be at least 30° C. The cheese supplies the ferment, and a regular process of fermentation takes place, in the course of which the sugar of the milk affords lactic acid; the latter as soon as produced is neutralised by the chalk, and calcium lactate is formed, while carbon dioxide escapes with effervescence. If the acid were not neutralised but allowed to accumulate in the liquid, the process would soon cease, as the special lactic ferment requires a nearly neutral liquid in which to develop. At the end of a fortnight action generally ceases, and the mixture is then very thick, owing to the presence of a large quantity of calcium lactate, which is only slightly soluble at the tempera-

ture. Add a liter and a half of water, stir well, boil the mixture for some time, and filter while hot. Calcium lactate slowly separates, and a considerable quantity may be obtained by evaporating the liquid to a small bulk.

When the calcium salt is treated with diluted sulphuric acid, and the solution filtered from calcium sulphate and evaporated, it leaves a syrupy acid liquid of sp. gr. 1·25, which cannot be distilled without decomposition : this is *lactic acid.*[1]

When this acid is boiled with diluted sulphuric acid, it breaks up into *aldehyde* and formic acid, unlike the first or hydracrylic acid when similarly treated.

Again, fermentation lactic acid when heated with hydriodic acid is reduced to the α-iodopropionic acid (derived from *secondary* propyl alcohol), thus :—

$$
\begin{array}{ccccc}
\text{CH}_3 & & \text{CH}_3 & & \text{CH}_3 \\
| & & | & & | \\
\text{CH}_2 & : & \text{CHI} & : & \text{CHOH} \\
| & & | & & | \\
\text{CH}_2\text{OH} & & \text{COOH} & & \text{COOH.}
\end{array}
$$
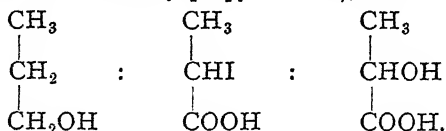
The synthesis of this particular lactic acid from *aldehyde* affords confirmatory evidence of its structure. If a mixture of aldehyde and hydrocyanic acid (or *ethidene cyanhydrin*, see page 88) with some hydrochloric acid be left in a warm place for some time,

---

[1] This acid, when heated to 150° in a current of air, is dehydrated and affords first *lactic anhydride* and then *lactide.*

Lactic anhydride	.	.	.	.	$C_6H_{10}O_5$
Lactide .	.	.	.	.	$C_6H_8O_5$
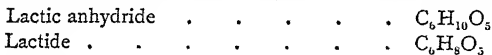
These obviously result from the dehydration of *two* molecules of acid. *Lactones* are anhydrides of *single* molecules of certain of the higher metameric acids of the series.

ammonium chloride and lactic acid are obtained, the latter being identical in properties with that produced by fermentation; the compound is therefore *ethidene lactic acid*, and is an *aldehydic* acid—

$$CH_3—COH + CNH + HCl + 2H_2O =$$
$$CH_3—CH(OH)—COOH + NH_4Cl.$$
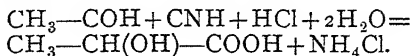
Similarly acetone can unite with hydrocyanic acid and form the cyanhydrine

$$(CH_3)_2C\diagdown\begin{matrix}OH\\CN.\end{matrix}$$
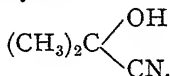
And this when allowed to stand with hydrochloric acid is slowly converted into an *oxybutyric acid* or *dimethoxyacetic acid*, which is a *ketonic* acid.

$$(CH_3)_2C\diagdown\begin{matrix}OH\\COOH.\end{matrix}$$
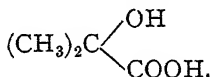
When oxidised this acid is resolved into acetone, carbon dioxide, and water.

Another distinctly *ketonic* acid, or rather its ethylic salt, is obtained by the elimination [1] of one molecule of ethyl alcohol from *two* molecules of ethyl acetate.

$$\begin{matrix}COOC_2H_5\\|\\CH_3\\\\COOC_2H_5\\|\\CH_3\end{matrix} = \begin{matrix}COOC_2H_5\\|\\CH_2\\|\\CO\\|\\CH_3\end{matrix} + HOC_2H_5.$$
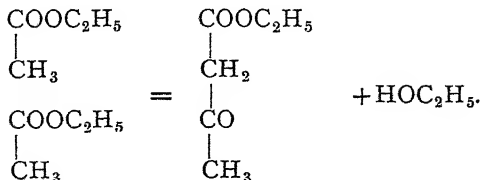
[1] Effected by the action of sodium on ethyl acetate; but the study of the changes involved would be much too difficult for the student at this stage.

By careful saponification we can produce the potassium salt of the acid, from which the latter is set free by careful addition of sulphuric acid ; ether dissolves the free acetoacetic acid, which is obtained as an oily liquid on evaporation of the ethereal solution. The relationship of this body to acetone is proved by the readiness with which it breaks up into acetone and carbon dioxide when heated with an alkali only. A comparison of the formulæ renders this intelligible :—

Acetoacetic acid, CH_3—CO—CH_2—$COOH$.
Acetone, CH_3—CO—CH_3.

Ethyl acetoacetate gives a violet colour with ferric chloride, and diabetic urine gives a similar coloration. Such urine, moreover, when distilled with baryta water, affords ethyl alcohol and acetone ; the latter can be best recognised in the distillate by the mercury test (see page 105). Geuther concludes from this evidence that diabetic urine contains the ester.

Ethyl acetoacetate has proved an important synthetic agent in the hands of Frankland and Duppa. When treated with sodium ethylate there is formed

$$CH_3—CO—CHNa—COOC_2H_5.$$

If this body be treated with methyl iodide, the sodium is exchanged for methyl—

$$CH_3—CO—CH(CH_3)—COOC_2H_5.$$
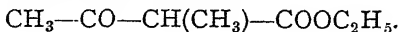
When decomposed by dilute potash (two molecules) this affords ethyl acetone, CH_3—CO—CH_2—CH_3, ethyl alcohol, and potassium carbonate.

If very strong potash be employed, potassium acetate, CH_3—COOK, alcohol and potassium propionate, C_2H_5—COOK, are produced. Thus we can build up higher ketones or higher acids.

It is not necessary to refer to the higher homologues of glycolic and lactic acids and their numerous isomers, as they are not yet of sufficient importance, but we shall now turn to the examination of the chief *amides* derivable from the acids of this series.

We know that the hydroxyl of acetic acid can be readily replaced by the NH_2 group with the production of acetamide—

$$
\begin{array}{ccc}
CH_3 & & CH_3 \\
| & : & | \\
COOH & & CONH_2 \\
\underbrace{\hspace{2cm}} & & \underbrace{\hspace{2cm}} \\
\text{Acetic acid.} & & \text{Acetamide.}
\end{array}
$$
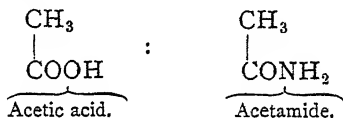
Glycolic acid should obviously afford an analogue by acetamide; and it does so, for when ethyl glycolate is heated with ammonia, *glycolamide* is produced, just as acetamide is obtained from ethyl acetate under similar conditions—

$$
\begin{array}{ccc}
CH_2OH & & CH_2OH \\
| & : & | \\
COOC_2H_5 & & CONH_2 \\
\underbrace{\hspace{2cm}} & & \underbrace{\hspace{2cm}} \\
\text{Ethyl glycolate.} & & \text{Glycolamide.}
\end{array}
$$
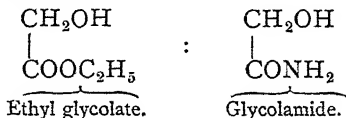
This amide is a somewhat sweet crystalline body which melts at 120°. It is much less soluble in alcohol than in water. From the mode of formation of glycolamide it is evident that the NH_2 group

replaces the hydroxyl of the COOH group of glycolic acid. But the *alcoholic hydroxyl* of the latter should also be replaceable by NH_2, in which case we should obtain a metameric amide or *amidoacetic acid* ; thus—

$$
\begin{array}{ccc}
CH_2OH & & CH_2NH_2 \\
| & : & | \\
CONH_2 & & COOH \\
\underbrace{} & & \underbrace{} \\
\text{Glycolamide.} & & \text{Amidoacetic} \\
& & \text{acid.}
\end{array}
$$
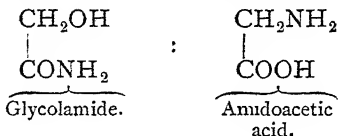
The mode of producing glycolic from chloracetic acid we have already employed (Experiment 725) suggests a method for the production of the metamer of glycolamide, viz. treatment of chloracetic acid with ammonia instead of potash—

$$
\begin{array}{cccc}
CH_2Cl & & CH_2NH_2 \\
| & +NH_3= & | & +HCl. \\
COOH & & COOH
\end{array}
$$
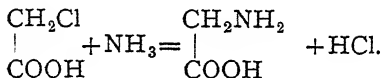
This change is readily effected.

Experiment 729.—Heat a solution of 5 grams of chloracetic acid with a large excess of ammonia for several hours. The liquid becomes brownish, and when evaporated to a small bulk affords crystals of ammonium chloride. The solution, when drained off and further concentrated, gives rhombic crystals of amidacetic acid,[1] which are, however, separated with difficulty from secondary products.

Amidacetic acid, $CH_2(NH_2)COOH$, is distinct in appearance from glycolamide, and, when pure, requires a much higher temperature for fusion. When

---

[1] This body is more readily obtained in a pure condition from *Hippuric acid* (see page 314).

heated alone it begins to discolour about 170°, and fuses above 200°. It has a sweetish taste, and is found to be identical in properties with a body long known under the name of gelatine sugar, or *glycocoll*. This is obtained by treating glue with twice its weight of strong sulphuric acid ; after standing for a week four volumes of water are added, and the liquid is boiled for two hours. When cool, excess of chalk is added, the calcium sulphate is filtered off, and the filtrate evaporated to a small bulk and set aside to crystallise. Glycocoll—*glycine* or *glycosine*, as it is now termed —slowly separates out, and with it another body, named *leucine*, which bears the same relation to *leucic* or *oxycaproic acid* that glycosine does to glycolic acid. They may be separated by boiling dilute alcohol, which dissolves glycosine and leaves leucine.

Glycosine in aqueous solution has a slightly acid reaction, and combines with metallic hydrates, forming feeble salts. When boiled with copper hydrate the latter dissolves, and the liquid affords beautiful blue crystals on cooling of $(CH_2(NH_2)—COO)_2Cu,H_2O$. The presence of the NH_2 group in glycosine seems to hold the acidic group $COOH$ in check, so that the new body forms feeble salts ; it likewise enables glycosine to act as a weak base towards acids, and so to perform a double rôle.

It is easy to produce glycolic acid from glycosine ; by treating the latter with nitrous acid the NH_2 group is replaced by OH, as when nitrous acid acts on a primary amine (see p. 128). In fact, 'glycolic' acid received its name owing to the fact that it was first obtained by the action of nitrous acid on

glycocoll,' or the gelatine sugar we now know to be a derivative of acetic acid.

Three metameric *lactic* amides are known ; two of them are analogous to the dicarbon compounds, and they are formed by similar methods, viz. *Lactamide*, obtained by the action of ammonia on ethyl lactate ; *Alanine*, or amido-propionic acid, a body analogous to glycosine, and prepared in a similar way from the α-iodopropionic acid, CH_3—CHI—$COOH$; while a third amide is formed when the β-iodopropionic acid, CH_2I—$CH(OH)$—$COOH$, is treated with ammonia—

$$
\begin{array}{ccccc}
CH_3 & & CH_3 & & CH_2NH_2 \\
| & & | & & | \\
CHOH & : & CHNH_2 & : & CHOH \\
| & & | & & | \\
CONH_2 & & COOH & & COOH \\
\underbrace{\hphantom{CONH_2}}_{\text{Lactamide.}} & & \underbrace{\hphantom{COOH}}_{\text{Alanine.}} & & \underbrace{\hphantom{COOH}}_{\text{Isoamide.}}
\end{array}
$$
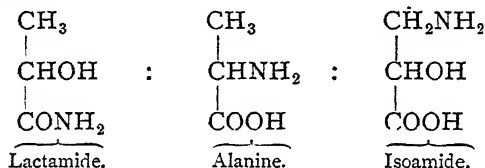
Alanine is also obtained by the action of hydrochloric acid on aldehyde ammonia and hydrocyanic acid—

$$(CH_3—CH)\begin{array}{c} \diagup NH_2 \\ \diagdown OH \end{array} + CNH + H_2O = \begin{array}{c} CH_3 \\ | \\ CHNH_2 \\ | \\ COOH \end{array} + NH_3.$$
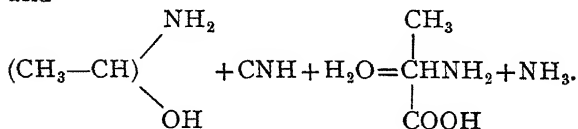
This resembles the synthesis of lactic acid from ethidene cyanhydrin (see p. 163).

The number of metameric amides increases as we ascend in series, but it is only necessary to mention

that the following glycosine homologues—or *alanines*, as they are often termed—are known :—

Amidoacetic Acid   . $CH_2(NH_2)$—COOH
(*Glycosine*).
Amidopropionic Acid . CH_3—CH(NH_2)—COOH
(*Alanine*)
Amidobutyric Acid   . C_2H_5—CH(NH_2)—COOH
Amidovaleric Acid   . C_3H_7—CH(NH_2)—COOH
Amidocaproic Acid   . C_4H_9—CH(NH_2)—COOH
(*Leucine*)

The last-named body, *Leucine*, or amidocaproic acid, is frequently met with in animal tissues, and is generally accompanied by a compound of similar constitution, viz. *Tyrosine*.[1] These bodies are commonly formed during the action of sulphuric acid on glue (as in the preparation of glycosine from it), or, better, on horn shavings. Small white nodules of impure leucine are often to be seen in museum specimens of animal tissues preserved in spirit ; the latter slowly precipitates the leucine in characteristic nodules made up of groups of needles. The solution in water gives a red colour with ferric chloride. If a nodule be heated with nitric acid and evaporated to dryness in a watchglass, the slightly coloured residue becomes yellow when treated with caustic soda.

In all the preceding cases glycosine and its homologues are formed by the action of *ammonia* on the corresponding chloro- or iodo-acid of the acetic series ; if, however, we use an *amine* instead of ammonia in acting on chloracetic acid, we get a *substituted glycosine*.

[1] C_6H_4OH—C_2H_3—$(NH_2)COOH$.

By the action of methylamine on chloracetic acid[1] we obtain methyl glycosine, which is identical with *Sarcosine*—a crystalline body obtained when flesh juice is boiled with baryta water.[2] With trimethyl-amine a *trimethyl-glycosine* is formed, which is identical with a basic substance extracted by Scheibler from the common beet in small quantity and named *Betaïne*. This is also identical with a body termed *oxyneurine* by Liebreich, and obtained by oxidation of choline (see p. 147). The relations of these bodies sufficiently appear from the following expressions, but the student will learn at a later stage that the formulæ do not fully represent the structure of the substances:—

$$
\begin{array}{ccccc}
CH_2NH_2 & & CH_2NH(CH_3) & & CH_2N(CH_3)_2 \\
| & : & | & : & | \\
COOH & & COOH & & COOCH_3 \\
\underbrace{\hspace{2cm}} & & \underbrace{\hspace{2cm}} & & \underbrace{\hspace{2cm}} \\
\text{Glycosine.} & & \text{Sarcosine.} & & \text{Betaïne.}
\end{array}
$$
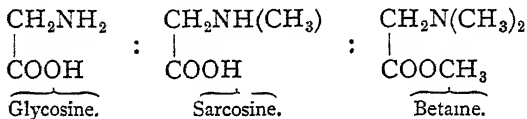
It is, therefore, possible to perform the syntheses of several complex products of animal and vegetable organisms with the aid of chloracetic acid.

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[1] Or, better, ethyl chloracetate.   [2] See *Creatine*, p. 206.

CHAPTER LVI.

DIBASIC ACIDS RELATED TO GLYCOLS — OXALIC, MALONIC, AND SUCCINIC ACIDS—THEIR SYNTHESES —MALIC AND TARTARIC ACIDS — THEIR DE-RIVATION FROM SUCCINIC ACID—PHYSICAL ISO-MERISM — PYRO-ACIDS — CITRIC ACID AND ITS PYRO-DERIVATIVES.

THE type of the second series of acids derivable from glycols is *oxalic acid.*

All the acids of the oxalic group are

DIBASIC ACIDS.

General formula $C_nH_{2n}(COOH)_2$.

Oxalic acid, a dicarboxyl without any attached hydrocanide residue, has been sufficiently described in the last chapter.

Malonic acid, $CH_2(COOH)_2$, can be obtained by the oxidation of the tricarbon glycol ; but a more convenient and instructive method for its production consists in heating *cyanacetic acid* with potash.

Experiment 730. — Potassium cyanacetate is formed in the first instance from monochloracetic acid. For this purpose dissolve 20 grams of the latter in about 50 c.cs. of water contained in a flask, just neutralise with potassium carbonate, and, having brought the flask under a flue with a powerful

draught, add 15 grams of pure potassium *cyanide*. On heating the mixture much poisonous hydrocyanic acid is evolved, so that the operation should not be undertaken unless a good draught chamber is available. Boil the liquid for half an hour, so as to complete the reaction, taking care to replace from time to time the water evaporated; at the end the solution contains potassium cyanacetate and chloride, resulting from the decomposition in which the chlorine and cyanogen change places.

$$\begin{array}{l} CH_2Cl \\ | \\ COOK \end{array} + KCN = \begin{array}{l} CH_2CN \\ | \\ COOK \end{array} + KCl.$$
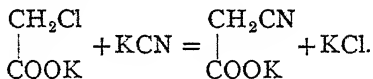
The conversion of the cyanacetate into malonate is effected by boiling with a considerable excess of caustic potash as long as ammonia is evolved; by this means the CN group, as usual, affords carboxyl, and potassium malonate results—

$$\begin{array}{l} CN \\ | \\ CH_2 \\ | \\ COOK \end{array} + H_2O + HOK = \begin{array}{l} COOK \\ | \\ CH_2 \\ | \\ COOK \end{array} + NH_3.$$
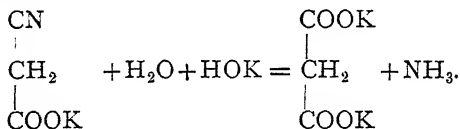
When the alkaline liquid is neutralised by hydrochloric acid and calcium chloride added, a precipitate of sparingly soluble calcium malonate separates, which is collected, washed with water, and dried. The free acid is obtained by digesting calcium malonate with half its weight of crystallised oxalic acid and water; calcium oxalate and free malonic acid result; the latter remains in solution and is filtered

off. When the filtrate is evaporated, crystals of the acid separate.

Malonic acid is soluble in alcohol and ether; the latter solvent serves to separate it from impurities. When pure it melts at 132°, and at a little higher temperature suffers a very remarkable decomposition, which we shall next examine.

Experiment 731.—Heat in a test-tube a few crystals of malonic acid; they fuse at 132°, as already stated, but when heated to about 150° gas is freely evolved, which can be poured over into a test-tube containing lime water and identified as carbon dioxide by the precipitate of chalk formed; the contents of the tube at the same time acquire the odour of *acetic acid*. Thus malonic acid, when heated, is resolved into carbon dioxide and acetic acid—

$$
\begin{array}{c}
\text{COOH} \\
| \\
\text{CH}_2 \\
| \\
\text{COOH}
\end{array}
=
\begin{array}{c}
\text{CH}_3 \\
| \\
\text{COOH}
\end{array}
+ \text{CO}_2.
$$
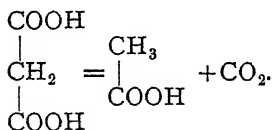
It is possible to replace the hydrogen of the CH_2 group in malonic acid by alcohol radicals[1] and so obtain substituted malonic acids, which latter suffer decomposition by heat into carbon dioxide and *homo-*

---

[1] The *modus operandi* consists in treating ethyl malonate with sodium ethylate, when an atom of H is replaced by Na and sodium ethyl malonate is formed. This, when treated with ethyl iodide, affords sodium iodide and $CH(C_2H_5)(COOC_2H_5)_2$, from which latter the substituted acid is obtained by saponification.

logues of acetic acid. Thus ethyl malonic acid affords carbon dioxide and a *butyric acid.*

$$\begin{array}{l} COOH \\ | \\ CH(C_2H_5) \\ | \\ COOH \end{array} = \begin{array}{l} CH_2C_2H_5 \\ | \\ COOH \end{array} + CO_2.$$
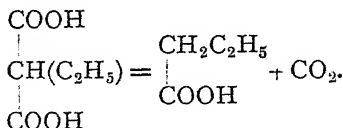
This is an important and effective synthetic method.

Succinic acid, $C_2H_4(COOH)_2$, can be obtained by the oxidation of the tetracarbon glycol. But its synthesis from ethylene dicyanide is of special interest and was first effected by Maxwell Simpson. Ethylene dichloride or bromide when treated with potassium cyanide affords the dicyanide, and the latter when boiled with alcoholic potash [1] yields potassium succinate and ammonia.

$$\begin{array}{l} CH_2-CN+H_2O+HOK \\ | \\ CH_2-CN+H_2O+HOK \end{array} = \begin{array}{l} CH_2-CO.OK \\ | \\ CH_2-CO.OK \end{array} + 2NH_3.$$
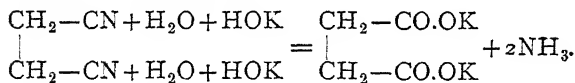
Succinic acid derives its name from the fact that it is met with in the acid liquid obtained in the destructive distillation of *Amber* (*Succinum*). It is present in all fermented alcoholic liquids, and occurs ready formed in unripe grapes, in common lettuce, and in several members of the poppy tribe. Succinic acid is a common product of the continued oxidation by nitric acid of the higher fatty acids and the natural

[1] Or better, according to Jungfleisch, by the gradual addition of nitric acid diluted with an equal volume of water.

fats. It is most conveniently obtained by reduction of the acid (malic acid) met with in the berries of the mountain ash (see Experiment 734).

Succinic acid is generally obtained in fine colourless crystals, which are easily soluble in water and in alcohol. It melts at 150° and by continued heating parts with a molecule of water and affords the anhydride—

$$
\begin{array}{l}
CH_2-CO \\
| \qquad\qquad\ >O. \\
CH_2-CO
\end{array}
$$
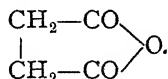
Experiment 732.—Neutralise a solution of succinic acid with ammonia and add ferric chloride solution ; a precipitate is formed which is at first yellowish and then becomes brown. Iron can be wholly precipitated as a basic salt from its solution by boiling with excess of ammonium succinate, and can in this way be separated from manganese, which is not precipitated by the reagent.

When succinic acid is heated in a pressure-tube to 120° with $1\frac{1}{2}$ times its weight of bromine, in presence of eight parts of water, monobromosuccinic acid is formed—

$$
\begin{array}{l}
CH_2-COOH \qquad\qquad CHBr-COOH \\
| \qquad\qquad +2Br = \quad | \\
CH_2-COOH \qquad\qquad CH_2-COOH.
\end{array}
$$
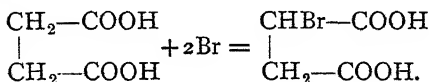
The bromo compound boiled with silver oxide and water (= silver hydrate) affords *malic acid*, or oxysuccinic acid, thus :—

$$
\begin{array}{l}
CHBr-COOH \qquad\qquad CH(OH)-COOH \\
| \qquad\qquad +AgOH = \quad | \\
CH_2-COOH \qquad\qquad CH_2-COOH.
\end{array}
$$
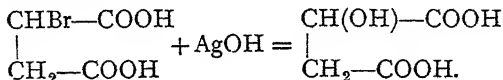
Malic acid is commonly present in half-ripe fruit such as apples, pears, cherries, and mountain-ash (rowan tree) berries. It is most easily prepared from the last.

Experiment 733.—Bruise and express the juice by pressure from a quantity of sour (*not* ripe) mountain-ash berries. Boil the liquid and clear by filtration, then add gradually thin milk of lime until the acid is just neutralised, and boil for some time. Calcium malate separates as a gritty powder; collect this, wash with cold water, and just dissolve with the aid of heat in nitric acid diluted with ten volumes of water. Acid calcium malate separates in cooling in fine crystals, which consist of

$$Ca(C_4H_5O_5)_2 8H_2O,$$
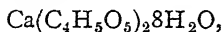
and require fifty parts of cold water for solution, though they are much more soluble in hot water. Lead malate is precipitated from the solution of the calcium salt by lead acetate ; the precipitate when well washed is suspended in water and the mixture saturated with sulphuretted hydrogen ; lead sulphide is formed and malic acid remains in solution, from which it can be obtained on evaporation, though with difficulty, in the crystalline form, as it is very deliquescent.

When malic acid is heated with strong hydriodic acid, it is reduced to succinic acid :—

$$\begin{array}{c} CH(OH)COOH \\ | \\ CH_2{-}COOH \end{array} + 2HI = \begin{array}{c} CH_2{-}COOH \\ | \\ CH_2{-}COOH \end{array} + H_2O + 2I$$
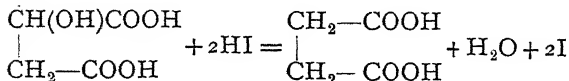
Its relationship to succinic acid is thus fully

IV.   N

established; moreover, crude calcium malate is the most convenient source of succinic acid.

Experiment 734.—In order to prepare succinic acid mix one part of the malate and eight of water, add about a fourth part of yeast, and keep the whole at a temperature of about 30°. Carbon dioxide is evolved, but ceases to escape after five or six days; during this process the malic acid is resolved into carbon dioxide, acetic and succinic acids. The last remains as calcium salt, which is washed and decomposed by sulphuric acid : the solution filtered from calcium sulphate affords crystals of succinic acid on evaporation. Three parts of calcium malate treated in this way afford one part of succinic acid.

Malic acid when heated above 150° loses water and affords two metameric acids, *fumaric* and *maleic* acids ; the latter contains an unsaturated carbon atom, and readily forms addition compounds :—

$$2 \begin{array}{l} CH_2(OH)\!-\!COOH \\ | \\ CH_2COOH \end{array} =$$

$$\underbrace{}_{\text{Malic acid.}}$$

$$\begin{array}{l} CH\!-\!COOH \\ \| \\ CH\!-\!COOH \end{array} + \begin{array}{l} CH_2\!-\!COOH \\ | \\ C\!-\!COOH \end{array} + 2H_2O.$$

$$\underbrace{}_{\text{Fumaric acid.}} \quad \underbrace{}_{\text{Maleic acid.}}$$

Malic acid obtained from fruit is optically active, and rotates the polarised beam to the right in strong or the left in dilute solutions. The malic acid synthetically prepared from succinic acid is optically

inactive, and rather less soluble than the active modification.   As no difference in constitution is known to exist between these varieties, they are termed *physical isomers* (see page 183).

When malic acid is oxidised by potassium bichromate and sulphuric acid, it affords malonic acid :—

$$
\begin{array}{l}
\text{CH(OH)—COOH} \\
\mid \qquad\qquad\qquad + 2O = \\
\text{CH}_2\text{—COOH}
\end{array}
\qquad
\begin{array}{l}
\text{COOH} \\
\mid \\
\text{CH}_2 \quad + \text{CO}_2 + \text{H}_2\text{O} \\
\mid \\
\text{COOH}
\end{array}
$$
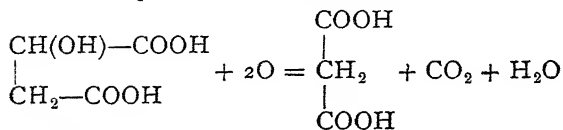
Malonic acid was first obtained in this way ; hence its name, indicating its derivation from malic acid.

Dibromosuccinic acid is obtained by heating succinic acid with three times its weight of bromine and water, as before.   When the new substance is boiled with silver oxide and water, dioxysuccinic or *tartaric acid* is formed.   The relationship of the latter to succinic and malic acids appears when the formulæ are compared:—

$$
\begin{array}{l}
\text{CH}_2\text{—COOH} \\
\mid \\
\text{CH}_2\text{—COOH}
\end{array}
:
\begin{array}{l}
\text{CH(OH)—COOH} \\
\mid \\
\text{CH}_2\text{—COOH}
\end{array}
:
\begin{array}{l}
\text{CH(OH)—COOH} \\
\mid \\
\text{CH(OH)—COOH}
\end{array}
$$
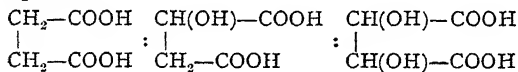
As tartaric acid is a comparatively stable substance, we conclude that each OH group is attached to a different carbon atom, for it has been already pointed out that any compounds we know which can be supposed to contain the system $C(OH)_2$ are extremely unstable.

Tartaric acid is reduced to succinic acid on heating with hydriodic acid.

It is particularly interesting to trace the simple

relations existing between the above three acids, which occur freely in the vegetable kingdom, and even in the same fruit; generally malic acid predominates in the unripe fruit, and tartaric acid is more commonly met with in ripe fruit. Tartaric acid is the chief acid present in ripe grapes. When the juice ferments in the manufacture of wine, impure hydrogen potassium tartrate, or *argol*, slowly separates as alcohol is formed, since the salt is but slightly soluble in dilute alcoholic liquids. This crude argol is the chief source of tartaric acid, which latter is prepared from it as follows.

Experiment 735.—Boil 20 grams of 'cream of tartar,' which is purified argol, with about 150 c.cs. of water; add powdered chalk gradually as long as effervescence is produced by the addition of fresh chalk. The following decomposition takes place :—

$$2(KHC_4H_4O_6) + CaCO_3$$
$$= CaC_4H_4O_6 + K_2C_4H_4O_6 + CO_2 + H_2O.$$
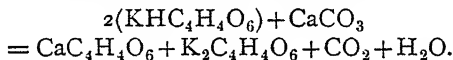
Calcium tartrate is precipitated, but half the tartaric acid remains in solution as neutral potassium tartrate. Now add to the turbid mixture calcium chloride solution in excess, when

$$K_2C_4H_4O_6 + CaCl_2 = CaC_4H_4O_6 + 2KCl.$$
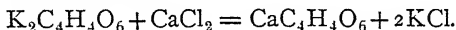
The remainder of the tartaric acid is thus separated as calcium salt. The whole precipitate is washed well with water by decantation. When sufficiently washed add 6 c.cs. of oil of vitriol, first mixed with about 50 c.cs. of water, to the moist precipitate; boil together, and filter. Calcium sulphate is formed, and tartaric acid is set free :—

$$CaC_4H_4O_6 + H_2SO_4 = H_2C_4H_4O_6 + CaSO_4.$$
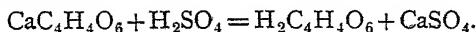
Filter the liquid, and evaporate; some calcium sulphate separates at first, and can be removed, but when the liquid is allowed to cool crystals of tartaric acid are obtained.

Tartaric acid, $H_2C_4H_4O_6$, occurs in colourless crystals having a strongly acid taste and reaction. They are easily soluble in water and alcohol. When lime water is added to a very dilute solution of the acid, no precipitate appears *until the acid is neutralised*; this test easily distinguishes it from oxalic acid, which is precipitated as calcium salt before the liquid is neutralised by calcium hydrate. When heated with strong sulphuric acid it is soon blackened, and an odour of burnt sugar is developed. A strong solution of a potassium salt added to a similar one of the acid causes a crystalline precipitate after a short time of hydrogen potassium tartrate. Pure tartaric acid does not precipitate calcium chloride. The common salts of tartaric acid met with are—*Cream of tartar,* $HKC_4H_4O_6$; *Rochelle salt,* $NaKC_4H_4O_6,4H_2O$; and *Tartar emetic,* $SbO,KC_4H_4O_6$.

Ordinary tartaric acid is optically active, being *dextrogyrate.* When the acid is heated to 165° with one-tenth of its weight of water in a pressure-tube for two hours, it affords *mesotartaric* acid, which is optically inactive, and whose hydrogen and potassium salt is more soluble than common 'cream of tartar.'

If the heating be continued for thirty hours, an acid is produced which crystallises in small needles, and is identical in properties with a substance also obtained in the manufacture of ordinary tartaric acid. This is paratartaric or *racemic acid*; it is distinguished

from the ordinary acid, not only by the appearance of
its crystals, but also by precipitating calcium chloride
solution.

Racemic acid is optically inactive, like mesotar-
taric acid, but Pasteur, in the course of a remarkable
investigation, was able to prove that racemic acid is a
compound of two optically active tartaric acids, one
of which turns the plane of polarisation to the *right*,
and is identical with ordinary tartaric acid, and the
other to the *left*.[1]   The former is destroyed when the
spores of the ferment *Penicillium glaucum* are allowed
to develop in a solution of ammonium racemate, and
the lævogyrate acid remains, as it is not nearly so
rapidly attacked by the organism.   Mesotartaric
acid is not divisible into two active acids.   When the
lævo- and ordinary dextro-gyrate acids are mixed in
molecular proportions, heat is developed, and in-
active racemic acid results.

The tartaric acid obtained by synthesis from di-
bromosuccinic acid is a mixture of mesotartaric and
racemic acids, according to Jungfleisch.

It is a remarkable fact that no difference in
chemical *constitution* has been detected between the
four modifications of tartaric acid ; they are therefore
said to be *physical isomers*.   It will be remembered
that we also noted the existence of *two* such isomers
of lactic acid, and *two* of malic acid.

It has been shown by Le Bel and Van't Hoff that
such physical isomerism is connected with the
presence of *asymmetric carbon* in the molecules ; that
is to say, with carbon whose four links or bonds are

[1] Lævogyrate.

united to four *different* radicals. Thus we can recognise one asymmetric carbon atom in *fermentation* lactic acid, and in malic acid :—

$$
\begin{array}{ccc}
\text{CH}_3 & & \text{CO}_2\text{H} \\
| & & | \\
\text{H—C—CO}_2\text{H} & : & \text{H—C—CH}_2\text{—CO}_2\text{H} \\
| & & | \\
\text{OH} & & \text{OH} \\
\text{Lactic acid.} & & \text{Malic acid.}
\end{array}
$$
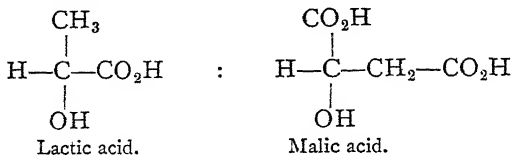
The optically active sarcolactic acid is identical in chemical structure with fermentation lactic acid, and therefore its molecule also contains an asymmetric carbon atom ; but the *fact* of the different action of the acids on polarised light remains to be accounted for. Van't Hoff ingeniously suggests that the diversity in optical properties is due to difference in arrangement of the radicals in space round the asymmetric carbon. Two distinct modes of grouping are possible, consequently two physical isomers are possible for each asymmetric carbon atom. Some conception of the meaning of this statement may be formed even if we represent the atomic grouping as below on a plane. Write the following formulæ for lactic acid on two separate slips of thin paper :—

$$
\begin{array}{cc}
\text{CH}_3 & \text{H} \\
| & | \\
\text{H—C—CO}_2\text{H} & \text{HO—C—CO}_2\text{H} \\
| & | \\
\text{OH} & \text{CH}_3
\end{array}
$$
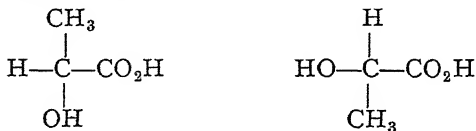
When the slips are superposed and held up to the light, it is found that the radicals cannot be made to coincide in any position of the slips.

Malic acid also contains one asymmetric carbon atom ; hence two modes of grouping are possible, and two modifications are known.

Tartaric acid includes *two* asymmetric carbon atoms :—

$$\begin{array}{ccc} & H & H \\ & | & | \\ HO_2C - & C - C & -CO_2H \\ & | & | \\ & OH & OH \end{array}$$
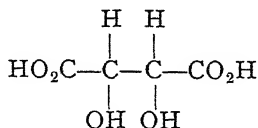
Consequently *four* distinct groupings are possible ; and this accords with the remarkable fact that four physical isomers of tartaric acid are known.

The action of heat on tartaric acid affords some interesting products, which we can only notice here. The acid melts at 140°, and undergoes molecular change into metatartaric acid. As the temperature rises the two following bodies are formed with loss of water :—

Ditartaric acid   .   .   . $C_8H_{10}O_{11}$
Tartaric anhydride .   .   . $C_8H_8O_{10}$
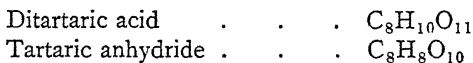
At a still higher temperature—about 300°—carbon dioxide and water are eliminated, and the two following acids result from the decomposition of three molecules of tartaric acid :—

$$\begin{array}{cc} CH_3 & \\ | & \\ CO & \qquad : \qquad CH_2 - COOH \\ | & \qquad\quad | \\ COOH & \qquad\quad CH(CH_3) - COOH \end{array}$$

Pyruvic or pyroracemic   Pyrotartaric or methyl-
        acid.   succinic acid.
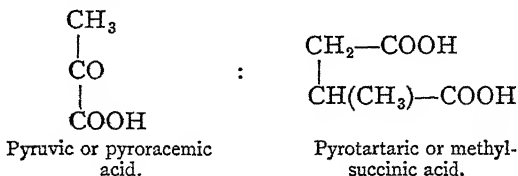
Pyruvic acid is a liquid which smells like acetic acid ; it unites with acid sulphites like a ketone, and may be regarded as acetone with one of the methyl groups replaced by COOH. On this view it is a *ketonic* acid. When treated with nascent hydrogen, pyruvic acid unites with two atoms and affords ordinary lactic acid.

Pyrotartaric acid is a crystalline acid which melts at 112° ; it is easily soluble in water and alcohol. When strongly heated it is resolved into butyric acid and carbon dioxide. Its synthesis has been effected by boiling the corresponding propylene cyanide with caustic potash.

Before passing from the consideration of this group of acids it is desirable to examine a remarkable *tribasic* acid which is related to them, and is often present in fruit juices ; it is known as *citric acid*, because principally derived from the fruit of the *citrus* tribe, of which the *lemon* and *lime* are our most familiar examples.

Citric acid, $H_3C_6H_5O_4$, is prepared in the following simple way from lemon juice :—

Experiment 736.—Express the juice from four good lemons, heat the liquid, and filter. Now boil the nearly clear liquid, and gradually add chalk in fine powder until the acidity of the liquid is completely neutralised ; then catch the precipitate—which is impure calcium citrate—on a filter and wash with boiling water. When thoroughly washed transfer the precipitate to a capsule and add water sufficient to make into a thin cream ; then pour in a weight of sulphuric acid equal to that of the chalk used in neutralising the juice in the first instance, and boil the mixture. Slightly soluble calcium sulphate is

formed and citric acid set free. The filtered liquid affords crystals of the impure acid on evaporation, and these can be purified by recrystallisation.

Pure citric acid occurs in fine colourless rhombic crystals which are readily soluble in water. The solution has a sour taste. Even when treated with considerable *excess* of lime water, no precipitate is formed until the liquid is boiled, when basic citrate of calcium is thrown down. The action of lime water thus serves to distinguish free citric acid from tartaric and oxalic acids.

Neutral potassium citrate contains $K_3C_6H_5O_4$, and a number of similar salts are obtainable ; hence, as already stated, citric acid is tribasic, and consequently contains three carboxyl groups. When citric acid is rapidly heated in a retort, it affords a distillate which readily gives the mercury reaction for *acetone*, described at p. 105, and that fact supplies some further evidence of the structure of the acid. In fact, Grimaux has succeeded in effecting the synthesis of citric acid from a symmetrical dichloracetone.[1] The latter unites directly with hydrocyanic acid, like most of the ketonic compounds. The relations of the cyano compound to the dichloracetone and acetone are shown by the following formulæ :—

$$
\begin{array}{ccccc}
CH_3 & & CH_2Cl & & CH_2Cl \\
| & & | & & | \\
CO & : & CO & : & C{<}^{OH}_{CN} \\
| & & | & & | \\
CH_3 & & CH_2Cl & & CH_2Cl \\
\end{array}
$$
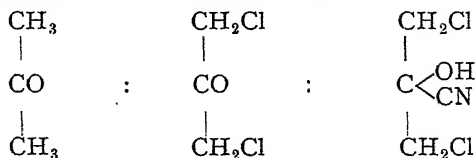
[1] A compound obtained by the removal of 2H from a dichlorhydrine derived from glycerine (see p. 226).

The CN group is then converted into carboxyl by heating with hydrochloric acid, and the dichloro-acid so obtained is made to afford the corresponding dicyano-acid, which latter by saponification yields citric acid. Thus :—

$$
\begin{array}{ccc}
\mathrm{CH_2Cl} & \mathrm{CH_2CN} & \mathrm{CH_2-COOH} \\
| & | & | \\
\mathrm{C}\!\!\begin{array}{c}\diagup\mathrm{OH}\\\diagdown\mathrm{COOH}\end{array} & : \quad \mathrm{C}\!\!\begin{array}{c}\diagup\mathrm{OH}\\\diagdown\mathrm{COOH}\end{array} & : \quad \mathrm{C}\!\!\begin{array}{c}\diagup\mathrm{OH}\\\diagdown\mathrm{COOH}\end{array} \\
| & | & | \\
\mathrm{CH_2Cl} & \mathrm{CH_2CN} & \mathrm{CH_2-COOH}
\end{array}
$$

Dichloroxybuty-   Dicyanoxybuty-   Citric acid.
ric acid.   ric acid.
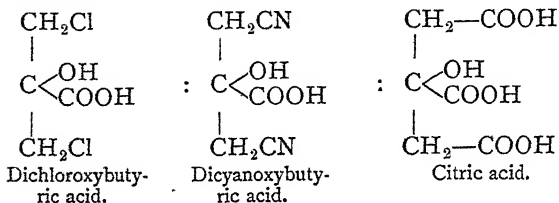
When citric acid is carefully heated in a flask, it melts at 176°, and then parts with a molecule of water. The residue left in the vessel after all white vapours cease to appear yields to ether a new tribasic acid, termed *aconitic acid*, because it is identical with an acid extracted from the *Aconitum napellus*, or monks-hood :—

$$
\begin{array}{ccc}
\mathrm{CH_2-COOH} & & \mathrm{CH-COOH} \\
| & & \| \\
\mathrm{C}\!\!\begin{array}{c}\diagup\mathrm{OH}\\\diagdown\mathrm{COOH}\end{array} & = & \mathrm{C-COOH} + \mathrm{H_2O} \\
| & & | \\
\mathrm{CH_2-COOH} & & \mathrm{CH_2COOH}
\end{array}
$$
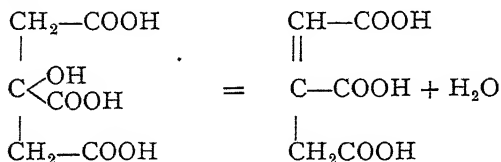
Both citric and aconitic acids, when more strongly heated, lose carbon dioxide and afford two isomeric acids—*citraconic* and *itaconic* acids, $C_6H_5O_4$. A third isomer—*mesaconic acid*—is formed when citraconic acid is boiled with dilute nitric acid.

All the above-mentioned derivatives of citric acid

are unsaturated, and readily unite with nascent hydro-
gen, the three isomeric acids affording pyrotartaric
acid, while aconitic acid gives *tricarballylic acid* :—

$$
\begin{array}{ll}
\text{CH}_2\text{—COOH} & \text{CH}_2\text{—COOH} \\
| & | \\
\text{C—COOH} \quad + \text{2H} = & \text{CH—COOH} \\
| & | \\
\text{CH}_2\text{—COOH} & \text{CH}_2\text{—COOH}
\end{array}
$$
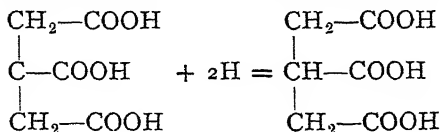
Another mode of producing tricarballylic acid will be
found at p. 235.

CHAPTER LVII.

THE amides of the oxalic series of acids are very readily formed in most cases, and the methods employed in their production are similar to those already used in the preparation of the corresponding compounds of the fatty series. The amide of oxalic acid, or *oxamide*, is a *diamide*, and is most rapidly obtained by the action of aqueous ammonia on ethyl oxalate.

Experiment 737.—Pour 3 or 4 c.cs. of ethyl oxalate into a beaker, dilute with five or six times its volume of alcohol, and add ammonia solution in excess. A white sub-crystalline mass soon separates ; this is oxamide, which results from the reaction—

$$\underbrace{\begin{matrix} CO-OC_2H_5 + NH_3 \\ | \\ CO-OC_2H_5 + NH_3 \end{matrix}}_{\text{Ethyl oxalate.}} = \underbrace{\begin{matrix} CO-NH_2 \\ | \\ CO-NH_2 \end{matrix}}_{\text{Oxamide.}} + 2HOC_2H_5$$
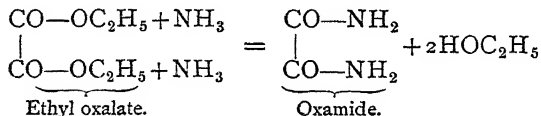
Oxamide is also obtained by heating neutral ammonium oxalate in a retort.[1]

$$\begin{matrix} CO-ONH_4 \\ | \\ CO-ONH_4 \end{matrix} = \begin{matrix} CO-NH_2 \\ | \\ CO-NH_2 \end{matrix} + 2H_2O$$
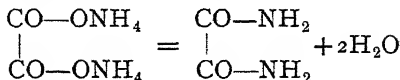
Collect the oxamide precipitated from the ethyl oxalate solution, wash it with cold water, and dry it.

Oxamide, $C_2O_2(NH_2)_2$, is a white powder which is not soluble in alcohol or water. When heated with the latter to 200°, it slowly combines with it and affords ammonium oxalate. When heated in the dry state, oxamide is partially decomposed, while a portion sublimes. When carefully heated with one molecule of mercuric oxide, oxamide loses one CO group and gives the diamide of carbonic acid, viz. *urea* (see page 194).

Oxalic acid being dibasic affords two ammonium salts—the neutral and the acid oxalate ; the former, when heated, is resolved into oxamide and water, the latter into water and a new body (whose purification is difficult) termed *oxamic acid* :—

$$\underbrace{\begin{matrix} CO-ONH_4 \\ | \\ COOH \end{matrix}}_{\substack{\text{Acid oxalate} \\ \text{of ammonium.}}} = \underbrace{\begin{matrix} CO-NH_2 \\ | \\ COOH \end{matrix}}_{\text{Oxamic acid.}} + H_2O.$$
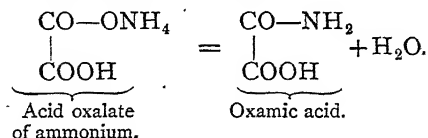
Oxamic acid is the type of a class of *amidated acids*, in which amidogen partly replaces the hydroxyl of a polybasic acid. Oxamic acid is a well-marked

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[1] Compare action of heat on ammonium acetate, page 114.

monobasic acid. It is a crystalline powder slightly soluble in cold water, but easily dissolved by boiling water and alcohol. When boiled for a long time with water, it slowly re-forms acid ammonium oxalate. With caustic alkalies it first forms salts, but by continued action an oxalate of the alkali metal is produced.

When the mixture of ethyl bases obtained in Hofmann's process (see page 124) is added to ethyl oxalate, triethylamine is unaffected, while ethylamine affords *diethyl oxamide*, and diethylamine *diethyl-oxamate of ethyl,* i.e. ethyl derivatives of the foregoing compounds :—

$$
\begin{array}{ccc}
\text{CO—NH(C}_2\text{H}_5) & & \text{CO—N(C}_2\text{H}_5)_2 \\
| & : & | \\
\text{CO—NH(C}_2\text{H}_5) & & \text{CO—OC}_2\text{H}_5 \\
\underbrace{\hspace{3cm}} & & \underbrace{\hspace{3cm}} \\
\text{Diethyl oxamide.} & & \begin{array}{c}\text{Diethyl-oxamate}\\\text{of ethyl.}\end{array}
\end{array}
$$
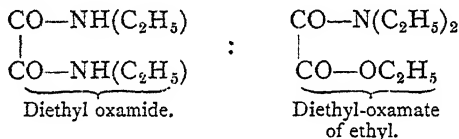
The excess of ethyl oxalate and triethylamine are distilled off. Water extracts the ethylated oxamide from the residue, and leaves the ethylic oxamate as an oily liquid. The amide can be crystallised out from the aqueous solution, or the latter may be at once distilled with caustic potash, when *ethylamine* is obtained and potassium oxalate remains :—

$$
\begin{array}{l}
\text{CO—NH(C}_2\text{H}_5) \\
| \hspace{2.5cm} +2\text{HOK} = \\
\text{CO—NH(C}_2\text{H}_5)
\end{array}
\quad
\begin{array}{l}
\text{CO—OK} \\
| \\
\text{CO—OK}
\end{array}
+2\left.\begin{array}{c}\text{C}_2\text{H}_5\\\text{H}\\\text{H}\end{array}\right\}\text{N}
$$
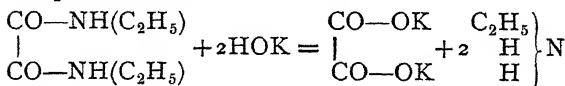
The ethylic oxamate, similarly treated, affords

$$
\begin{array}{l}
\text{CO—N(C}_2\text{H}_5)_2 \\
| \hspace{2.5cm} +2\text{HOK} = \\
\text{CO—OC}_2\text{H}_5
\end{array}
\quad
\begin{array}{l}
\text{CO—OK} \\
| \\
\text{CO—OK}
\end{array}
+\left.\begin{array}{c}\text{C}_2\text{H}_5\\\text{C}_2\text{H}_5\\\text{H}\end{array}\right\}\text{N}
$$
$$+ \text{HOC}_2\text{H}_5.$$
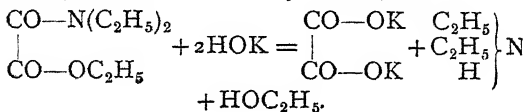
Analogous amidic compounds are derivable from the higher acids, malonic, succinic, &c.   The amides are, however, best obtained by the action of ammonia on the esters, as the decomposition of the neutral ammonium salts generally proceeds too far, and affords an *imide* rather than an amide.   Hence *succinimide* is easily prepared as follows.

Experiment 738.—Heat about 20 grams of dry ammonium succinate in a small retort ; when the temperature reaches 200°, decomposition commences, water distils over, and ammonia is evolved.   On raising the temperature succinimide distils over and crystallises from the liquid in the receiver in fine rhombohedral plates with one molecule of water, which it readily parts with at 100°.   It is probable that there are two stages in the decomposition of the succinate : during the first stage *succinamide* is formed with loss of water :—

$$CH_2—CO—ONH_4 \atop CH_2—CO—ONH_4 = \begin{array}{l} CH_2—CO—NH_2 \\ CH_2—CO—NH_2 \end{array} + 2H_2O$$
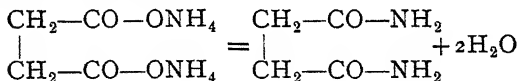
and during the second stage *succinimide* is produced with loss of ammonia, thus :—

$$\underbrace{CH_2—CO—NH_2 \atop CH_2—CO—NH_2}_{\text{Succinamide.}} = \underbrace{CH_2—CO \atop CH_2—CO}_{\text{Succinimide.}}{\Large >}NH + NH_3$$
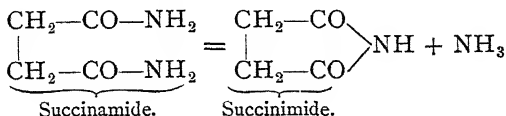
The anhydrous succinimide fuses at 125° and boils at 288°.   Its solution has an *acid* reaction, and it readily exchanges its imide hydrogen for metals such as silver and mercury.

Malic acid, or hydroxysuccinic acid, affords an amide and an amic acid, to which the compounds *Asparagine* and *Aspartic acid*, met with in asparagus and very generally in vegetable juices, bear the relations indicated by the following formula :—

$$
\begin{array}{cccc}
CO-NH_2 & CO-NH_2 & CO-NH_2 & CO-OH \\
C_2H_3(OH) : & C_2H_3(NH_2) : & C_2H_3(OH) : & C_2H_3(NH_2) \\
CO-NH_2 & CO-OH & CO-OH & CO-OH \\
\text{Malamide.} & \text{Asparagine.} & \text{Malamic acid.} & \text{Aspartic acid.}
\end{array}
$$
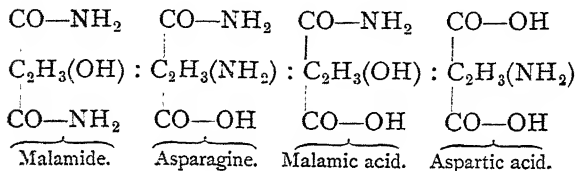
Asparagine is metameric with malamide and aspartic with malamic acid. Asparagine is a colourless crystalline body, which is almost insoluble in alcohol, but is moderately soluble in water. When boiled with an acid it affords aspartic acid and ammonia : hence it is to be regarded as an amide of aspartic acid.

It has been already pointed out (see page 190) that when oxamide is gently heated with one molecule of mercuric oxide one CO group is eliminated, and *urea* is formed ; thus—

$$
\begin{array}{l}
CO-NH_2 \\
| \qquad\qquad + HgO = CO\Big\langle{}^{NH_2}_{NH_2} + CO_2 + Hg. \\
CO-NH_2 \\
\underbrace{}_{\text{Oxamide.}} \qquad\qquad \underbrace{}_{\text{Urea.}}
\end{array}
$$
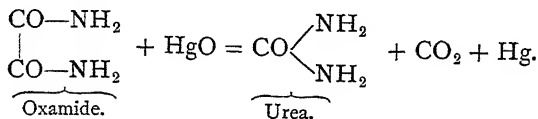
This is not a good mode of producing urea, but it is of theoretic interest as a means of passing from the amide of oxalic acid to the amide of hypothetical

carbonic acid,[1] i.e. to *carbamide* or urea. The same product is obtained when carbonyl chloride acts upon ammonia.

$$COCl_2 + 2NH_3 = CO(NH_2)_2 + 2HCl.$$
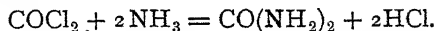
So that the relation of the amide to carbonic acid is clear.

Since the salts of carbonic acid are those of a dibasic acid like oxalic acid, we should expect to obtain not only an amide (carbamide), but a related amic acid; thus—

$$CO\begin{array}{l} \diagup NH_2 \\ \diagdown NH_2 \end{array} \qquad : \qquad CO\begin{array}{l} \diagup NH_2 \\ \diagdown OH \end{array}$$

$$\underbrace{\qquad\qquad}_{\text{Carbamide.}} \qquad\qquad \underbrace{\qquad\qquad}_{\text{Carbamic acid.}}$$
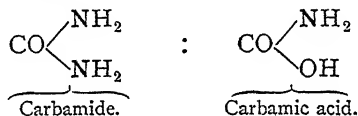
We do not know free carbamic acid, but its ammonium salt is easily obtained by shaking up the 'Sesquicarbonate of Ammonia' with alcohol; the latter dissolves out the carbamate, while the ammonium hydrogen carbonate is left as an insoluble residue (see Experiment 661). The carbamate can be obtained by careful evaporation. It is doubtless formed during the process of manufacture by the action of heat on ammonium carbonate, which changes to carbamate with the loss of the elements of water.

$$CO\begin{array}{l} \diagup ONH_4 \\ \diagdown ONH_4 \end{array} = CO\begin{array}{l} \diagup NH_2 \\ \diagdown ONH_4 \end{array} + H_2O.$$
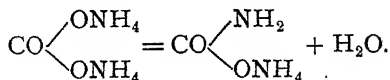
[1] If a methylene glycol, $CH_2(OH)_2$ can exist, it should give carbonic acid, $CO(OH)_2$, on oxidation, in which case the latter would be the first member of the glycolic or lactic series of acids, though dibasic.

By cautiously heating ammonium carbamate, Basaroff has succeeded in converting it into carbamide or urea.

$$CO\!\!\begin{array}{c}\diagup NH_2 \\ \diagdown ONH_4\end{array} = CO\!\!\begin{array}{c}\diagup NH_2 \\ \diagdown NH_2\end{array} + H_2O.$$
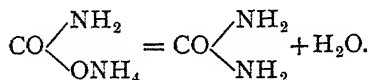
Just as ethyl oxalate affords oxamide by the action of ammonia, so ethyl carbonate yields carbamide, though not so easily.

Ethyl carbonate is obtained either by the action of ethyl iodide on silver carbonate, or better by digesting ethyl oxalate with about one-eighth of its weight of sodium ethylate; in the latter case carbon dioxide is evolved, and on addition of water the carbonate separates as a liquid slightly lighter than water, sp. gr. 0·98, which boils at 126°.

Experiment 739.—Mix equal volumes of ethyl carbonate and ammonia solution, and allow to stand in the cold; the carbonate gradually dissolves, and the liquid affords, on evaporation at a lower temperature, beautiful crystals of *ethyl carbamate* or *urethane*, resulting from the reaction—

$$CO\!\!\begin{array}{c}\diagup OC_2H_5 \\ \diagdown OC_2H_5\end{array} + NH_3 = CO\!\!\begin{array}{c}\diagup NH_2 \\ \diagdown OC_2H_5\end{array} + HOC_2H_5.$$
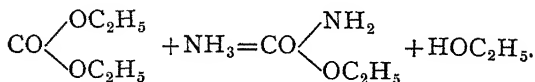
This substance is now much used in medicine as a hypnotic instead of chloral. It fuses at 52° and boils at 180°. On cooling it solidifies to a pearly crystalline mass. When *heated* with excess of am-

monia[1] it is converted into urea and ethyl alcohol :
hence its name *urethane*—

$$CO{<}^{NH_2}_{OC_2H_5} + NH_3 = CO{<}^{NH_2}_{NH_2} + HOC_2H_5$$

$\underbrace{}_{\text{Urethane.}} \qquad\qquad \underbrace{}_{\text{Urea.}}$
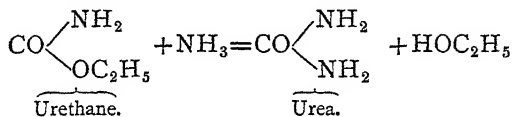
Carbamide, or urea, is, however, most easily
prepared from human urine, of which it forms one to
two per cent.

Experiment 740.—Evaporate half a liter of fresh
urine to about one-fifth of its original volume, and
allow it to cool. Pour the concentrated urine into a
rather tall beaker, and cool the latter by resting it in
a freezing mixture of hydrochloric acid and crystallised
sodium sulphate. Similarly cool an equal volume of
colourless nitric acid, then pour the latter into the
urine and mix quickly. Some effervescence, due to
the decomposition of a little ammonium carbonate,
generally takes place, and then brownish crystals of
urea nitrate, CON_2H_4,HNO_3, separate, as the latter
is very slightly soluble in free nitric acid, though
easily dissolved by pure water. The semi-solid mass
is thrown on a funnel whose neck is partially closed
by fibrous asbestos, and the acid liquid is drained
away. The residue is then washed with a little ice-
cold water, removed, and air-dried on porous bricks.
When quite dry the nitrate will keep indefinitely.

---

[1] If cyanic acid (which may be regarded as the *imide* of
carbonic acid, $CO = NH$) be allowed to act on urethane, *ethyl
allophanate* is produced, $CO{<}^{NH—CO—NH_2}_{OC_2H_5}$

In order to separate urea from the nitrate mix the latter with a little warm water, and add barium carbonate until effervescence no longer takes place on further addition. Evaporate the whole on the water-bath to dryness, and digest the residue with alcohol, adding at the same time a little freshly ignited animal charcoal to absorb some brown colouring matter, then filter the alcoholic solution and evaporate it, when deliquescent crystals of urea will be obtained. The barium carbonate decomposes the nitrate in the following way :—

$$2[CON_2H_4,HNO_3]+BaCO_3=2CON_2H_4 \\ +Ba(NO_3)_2+CO_2+H_2O.$$
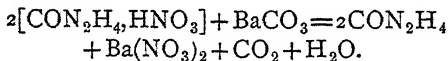
Barium nitrate and excess of carbonate are insoluble in alcohol; only the urea dissolves.

Urea is the chief form in which the nitrogen arising from tissue waste is eliminated by man, and its synthesis was the first one effected of any substance produced by a living organism. This important synthesis was made by the late Professor Wöhler in 1828, and gave the first blow to the preconceived notion that compounds formed under the influence of ‘vital force’ are not produced in accordance with the ordinary laws of chemistry. The nature of this synthesis has been already indicated at page 208 of Part II. (4th ed.); but it is desirable to enter into more detail here.

Experiment 741.—Prepare some potassium isocyanate by first heating a mixture of 20 grams of dehydrated potassium ferrocyanide with 7 grams of potassium carbonate in a Hessian crucible, as in

the preparation of potassium cyanide, Experiment 266*h*. When in tranquil fusion stir in little by little 36 grams of dry red lead until the whole has been added, then let the crucible cool, break it, and separate from metallic lead the solid mass of impure iso-cyanate, KNCO.

The latter is dissolved in sufficient boiling water, 20 grams ammonium sulphate are added, and the liquid is evaporated to dryness on the water-bath. During this process the potassium cyanate and ammonium sulphate react as follows :—

$$2KNCO + (NH_4)_2SO_4 = 2NH_4NCO + K_2SO_4.$$
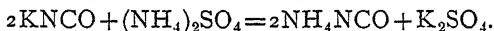
The saline compound ammonium cyanate then undergoes molecular rearrangement, and the metameric body urea only is found in the residue, from which it is extracted by alcohol and purified by recrystallisation :

$$NH_4NCO = CO \Big\langle \begin{matrix} NH_2 \\ NH_2 \end{matrix}$$
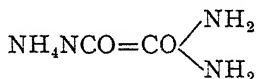
Pure Urea is obtained in colourless crystals which are deliquescent in moist air ; it is easily soluble in water and alcohol, but very slightly in ether. It melts at 130°, and at a higher temperature is rapidly decomposed into cyanuric acid and a body termed *biuret.*

Experiment 742.—Carefully heat a few crystals of urea in a test-tube beyond the melting-point of the compound, and until ammonia is rather freely evolved, then allow to cool. On the addition of warm water most of the cyanuric acid, $H_3C_3N_3O_3$, formed is left,

and *biuret* [1] dissolves. The latter is derived from two molecules of urea by the elimination of a molecule of ammonia—

$$CO\begin{cases} NH_2 \\ NH_2 \end{cases} \qquad CO-NH_2$$
$$= \quad NH \qquad +NH_3.$$
$$CO\begin{cases} NH_2 \\ NH_2 \end{cases} \qquad CO-NH_2$$
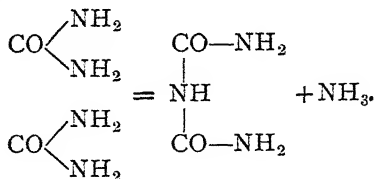
Add to the contents of the test-tube a few drops of copper sulphate solution and then excess of caustic soda ; a violet or red colour is produced, which is due to the biuret present. This reaction serves for the recognition of urea, owing to the ready conversion of the latter into biuret.

Urea acts as a rather feeble base toward acids, the most characteristic salts being the nitrate already prepared and the oxalate, $(CON_2H_4)_2H_2C_2O_4$, which readily separates on the addition of solution of oxalic acid to one of urea. The hydrochlorate is not formed in solution, but is produced by the action of gaseous hydrochloric acid on urea.

Mercuric nitrate solution precipitates urea. The composition of this precipitate depends on the mode of operating ; but when the mercury solution is added to excess of urea the compound $(CON_2H_4)_2(HgO)_3$ is thrown down. Liebig founded on this fact a method for the estimation of urea in urine. The amide combines with a large number of salts.

[1] Biuret is more abundantly formed when chlorine is led over melted urea.

When heated with water, especially in presence of alkali, ammonium carbonate results :—

$$CO\begin{cases} NH_2 \\ NH_2 \end{cases} + 2H_2O = CO\begin{cases} ONH_4 \\ ONH_4 \end{cases}$$
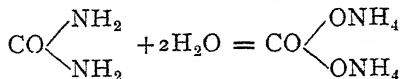
If barium hydrate be present, barium carbonate is formed and ammonia set free ; each molecule of the carbonate produced corresponds to a molecule of urea decomposed. This is the foundation of a method devised by Bunsen for the estimation of urea.

Experiment 743.—To a solution of urea add a few drops of nitrous acid. Note that gas is immediately evolved, which is nitrogen mixed with carbon dioxide, resulting from the reaction—

$$CON_2H_4 + 2HNO_2 = 2N_2 + CO_2 + 3H_2O.$$
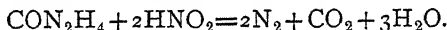
Experiment 744.—Add to some urea solution strongly alkaline sodium hypobromite ; gas is at once evolved, which is wholly nitrogen, if the solution contained excess of caustic alkali—

$$CON_2H_4 + 3NaOBr + 2NaOH = N_2 + 3NaBr$$
$$+ Na_2CO_3 + 3H_2O.$$
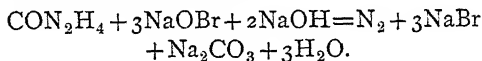
The volume of nitrogen *approximately* corresponds to the urea decomposed. This is the principle of the Davy[1]-Knop method for the estimation of urea. Ureas containing alcohol radicals [2] can be obtained

[1] The process is due to Dr. Edmund Davy, who used hypochlorite to decompose the urea. The hypobromite acts more regularly.

[2] Ureas containing *acid* radicals instead of amidic hydrogen are obtained by the action of acid chlorides on urea, viz. acetyl chloride affords acetyl urea.

(1) by heating cyanates of the ammonium bases; thus ethyl-urea, $CON_2H_3(C_2H_5)$, is formed from ethyl-ammonium cyanate; and (2) by the action of ammonia on an isocyanic [1] ester or *carbimide* (see page 121). Ethyl iso-cyanate and ammonia afford ethyl-urea—

$$C_2H_5-CO:N+NH_3=CO \diagdown \!\!\!\!\! \diagup \begin{array}{c} NHC_2H_5 \\ NH_2 \end{array}$$
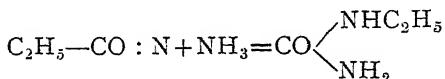
Ethyl iso-cyanate and ethylamine give diethyl-urea, or with diethylamine we obtain triethyl-urea. Triethylamine does *not* afford the tetrethyl-urea; but the latter body is produced when carbonyl chloride acts on diethylamine dissolved in ligroine or light petroleum spirit—

$$COCl_2+2(C_2H_5)_2HN=CO \diagdown \!\!\!\!\! \diagup \begin{array}{c} N(C_2H_5)_2 \\ N(C_2H_5)_2 \end{array} +2HCl.$$
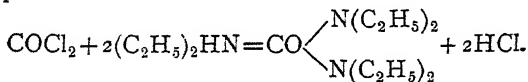
[1] Normal cyanic esters do not afford ureas.

CHAPTER LVIII.

THIOCARBAMIDE OR THIOUREA—ITS PREPARATION—
ADDITION PRODUCTS—ITS DESULPHURATION—
CYANAMIDE—DICYANDIAMIDE—MELAMINE—DICY-
ANODIAMIDINE — GLYCOCYAMINE — CREATINE —
CREATININE—GUANIDINE—MELLONE—AMMONIUM
THIOCARBAMATE—THIOURETHANE—XANTHATES—
ETHYL THIOCYANATE AND THIOCARBIMIDE —
MUSTARD OILS—SUBSTITUTED THIOUREAS—URIC
ACID—MUREXIDE TEST—ALLOXAN—MESOXALIC
ACID—ALLOXANTIN—PARABANIC AND OXALURIC
ACIDS—ALLANTOIN — XANTHINE — THEOBROMINE
AND CAFFEINE—SYNTHESIS OF CAFFEINE.

THE existence of well-known sulphur analogues of oxygen compounds led chemists to anticipate the production of a sulphur urea, or *thiocarbamide*, corresponding to ordinary urea or carbamide—

$$CO \Big\langle {NH_2 \atop NH_2} \qquad : \qquad CS \Big\langle {NH_2 \atop NH_2}$$

$$\underbrace{\phantom{CO<NH_2}}_{\text{Carbamide.}} \qquad\qquad \underbrace{\phantom{CS<NH_2}}_{\text{Thiocarbamide.}}$$

Liebig, Wöhler, and many other chemists sought to prepare thiocarbamide, but failed to do so, and were led to adopt the hypothesis that ordinary ammonium

thiocyanate [1] (see Part II. p. 208) was the urea, notwithstanding the marked saline character of the compound. The hypothesis in question was invalidated in 1868 by the writer's discovery of true thiocarbamide, which latter can be produced in large quantity by the following method :—

Experiment 745.—Place in a Florence flask about 30 grams of ammonium thiocyanate and heat gently. The salt fuses at 147° to a pale yellowish liquid. Now hang a thermometer with its bulb in the liquid, and heat the latter to 170° for half an hour. Allow the melt to cool down until just about to solidify, then add 40 to 50 c.cs. of *hot* water, mix rapidly, and filter through a little cotton wool, to separate a black substance always formed in the process. The liquid affords beautiful long silky needles of thiocarbamide after some time ; these are to be removed, rapidly washed with some *cold* water from unchanged thiocyanate, and then dissolved in a little hot water, from which the urea separates in short rhombic crystals. Heat determines the molecular rearrangement of the thiocyanate—

$$NH_4NCS = CS\begin{cases} NH_2 \\ NH_2 \end{cases}$$
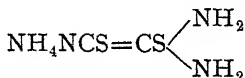
Thiourea, or *thiocarbamide*, CSN_2H_4, melts at 149° ; it dissolves in about eleven parts of water at 15°. It is easily soluble in alcohol, but is scarcely soluble in ether, benzene, or chloroform. Its solution gives only a faint red coloration with ferric chloride, and is thus easily distinguished from one of un-

[1] Isothiocyanate, $NH_4—N = CS$, commonly called sulphocyanide of ammonium.

changed thiocyanate. When its aqueous solution is
mixed with strong colourless nitric acid, a sparingly
soluble nitrate, $CSN_2H_4HNO_3$, separates, just as in
the case of ordinary urea ; like the latter, thiocarb-
amide unites with other acids, metallic oxides, and
salts.   Large numbers of such compounds have been
prepared and described, but cannot be referred to
here ; it is, however, desirable to point out that thio-
carbamide, unlike ordinary carbamide, can combine
directly with methyl and ethyl iodides, and affords
compounds in which sulphur acts as a tetrad, as in
the sulphine compounds mentioned on page 98.[1]
We can obtain in this way

$$CSN_2H_4,CH_3I \quad \text{and} \quad CSN_2H_4,C_2H_5I.$$
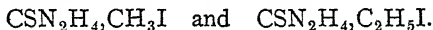
Thiocarbamide is easily desulphurised, and in an
interesting manner.

Experiment 746.—To a solution of the amide
contained in a clean test-tube add an alkaline solution
of lead tartrate,[2] and heat.   The liquid gradually
assumes a brownish colour, and then quickly becomes
turbid ; on continuing to heat a beautiful specular
layer of lead sulphide firmly attaches itself to the
bottom and sides of the tube.   When slowly de-
posited the lead sulphide not only resembles in

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[1] For a similar reason thiocarbamide can afford derivatives
of condensed ureas. The most complex body of this order yet
known is one lately obtained by the writer, containing four
thiocarbamide groups.

[2] Equal weights of lead nitrate and Rochelle salt are
separately dissolved in water, the solutions then mixed, and the
precipitated lead tartrate dissolved by the addition of sufficient
caustic soda.

appearance, but assumes a crystalline structure similar to that of some specimens of the mineral *galena*, PbS. Hence a true synthesis of galena can be effected by means of thiocarbamide.

The decomposition which takes place is represented by the following equation :—

$$CS\begin{cases}NH_2 \\ NH_2\end{cases} + PbO = PbS + \underbrace{CN-NH_2}_{Cyanamide.} + H_2O$$

$$\underbrace{\hphantom{CS\begin{cases}NH_2 \\ NH_2\end{cases}}}_{Thiocarbamide.}$$
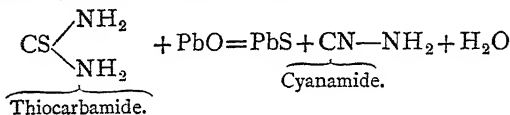
When thiocarbamide is desulphurised in aqueous solution by recently precipitated mercuric hydrate, added in small successive quantities [1] until the whole of the sulphur is removed as mercuric sulphide, the cyanamide can be easily obtained from the filtered liquid by careful evaporation at a low temperature. This is the best method for the production of cyanamide, but it can also be formed by the action of ammonia on cyanogen chloride.

$$CN-Cl + NH_3 = CN-NH_2 + HCl.$$
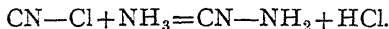
Cyanamide is a feebly basic body ; it occurs in deliquescent crystals, which melt at 40° ; they are easily soluble in ether, and when sulphuretted hydrogen gas is passed into the solution, thiocarbamide is re-formed [2]—

$$CN-NH_2 + H_2S = CS\begin{cases}NH_2 \\ NH_2\end{cases}$$
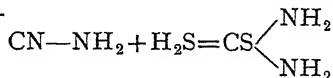
[1] Lumps of ice must be added from time to time in order to keep the temperature down, else the cyanamide would polymerise.

[2] When hydrogen *selenide* is passed through the ethereal solution, *selenocarbamide* is formed.

When ammonia silver nitrate is added to a solution of cyanamide, a very characteristic yellow precipitate is obtained by diargentic cyanamide, $CN—NAg_2$, or, probably, cyandiimide, $C(NAg)_2$.

Dry cyanamide readily polymerises when heated, and affords *dicyandiamide*, which is insoluble in ether—

$$H_2N—(NH)C—NH—CN.$$
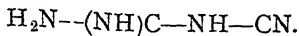
On heating to a temperature above 150° three molecules of cyanamide unite, and another polymer, *cyanuramide* or *melamine*, $C_3N_3(NH_2)_3$, is produced. When one molecule of water is present, *dicyanodiamidine* is formed—

$$H_2N—(NH)C—NH—CO—NH_2.$$
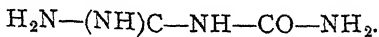
By the action of another molecule of water it breaks up into two molecules of urea.

Cyanamide readily forms addition compounds with glycosine and with substituted glycosines. Thus, when heated with glycosine in presence of a little ammonia, it affords *glycocyamine*—

$$CH_2—NH—C=NH$$
$$| \qquad\qquad |$$
$$COOH \qquad NH_2$$
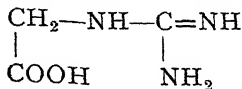
But if *sarcosine* (see page 171) be substituted for glycosine the base *creatine*—

$$CH_2—N(CH_3)—C=NH$$
$$| \qquad\qquad\qquad |$$
$$COOH \qquad\qquad NH_2$$
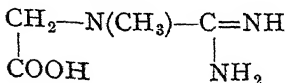
is obtained.[1] When the latter is heated with diluted sulphuric acid, a molecule of water is eliminated, and we produce *creatinine*—

$$CH_2—N(CH_3)—C=NH$$
$$CO————————NH.$$
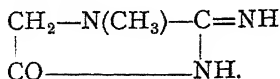
Of the two substances just mentioned creatine is present in *flesh-juice*, and is easily separated from 'Liebig's extract of beef,' previously diluted with 15 parts of water. Add basic lead acetate until no further precipitate appears, filter, pass sulphuretted hydrogen through the filtrate to remove excess of lead; filter again and evaporate, when crystals of creatine separate. Creatine is present in small quantity in human urine.

Having now dealt with the desulphuration of thiocarbamide, and with some of the chief relations of the derived cyanamide, we shall refer shortly to the action of heat on thiourea.

Experiment 747.—Heat in a test-tube a small quantity of the urea, and note that when the temperature is raised much beyond the melting-point a sulphuretted smell is developed, and ammonium thiocarbonate, $(NH_4)_2CS_3$, sublimes, while a whitish residue is left, which chiefly [2] consists of the thio-

[1] When creatine is heated with baryta water, it breaks up into sarcosine and *urea*, the latter doubtless resulting from the hydration of cyanamide, as already explained.

. [2] Melamine (see last page) and melam (or melamine imide), $(C_3N_3(NH_2)_2)_2NH$, are other products.

cyanate of a new and powerful base termed *guanidine*,[1] CN_3H_5, obtainable in colourless crystals easily soluble in water. When guanidine is heated with an acid, it assimilates the elements of water and breaks up into urea and ammonia ; hence its structure is probably

$$C{=}NH \begin{cases} NH_2 \\ \\ NH_2 \end{cases}$$
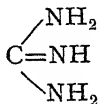
It is noteworthy that guanidine hydrochlorate is obtained by heating chloroform (see p. 95) with excess of ammonia. Large numbers of compounds of this highly nitrogenised base have been prepared, but the most interesting is the carbonate, which is easily obtained by double decomposition when potassium carbonate and guanidine thiocyanate are mixed in solution in molecular proportions, and the liquid evaporated to dryness. Alcohol extracts potassium thiocyanate from the residue and leaves guanidine carbonate, CN_3H_5,HCO_3. The thiocyanate or thiourea, if heated to a very high temperature out of contact with air, leaves a bulky yellow powder, which contains C_9N_{12}, and is named *mellone*.

Hence, when we compare the action of heat on the two primary ureas, we find that biuret and cyanuric acid are the principal products from ordinary urea, while thiourea chiefly affords guanidine thiocyanate, and the amide of cyanuric acid—cyanuramide, or melamine.

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[1] So named because first obtained by oxidation of *guanine*, derived from guano (see p. 217).

We already know [1] that carbon disulphide unites with alkaline sulphydrates and forms thiocarbonates, which are strictly analogous to the oxygen compounds. Comparing the ammonium salts we have

$$(NH_4)_2CO_3 \quad \text{and} \quad (NH_4)_2CS_3.$$
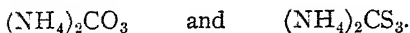
As the former readily affords ammonium carbamate and water, the thiocarbamate should afford ammonium thiocarbamate and sulphuretted hydrogen ; and this change can be effected. But the thiocarbamate can be directly prepared in the following easy way :—

Experiment 748.—Mix in a flask 20 c.cs. of carbon disulphide with five times its volume of alcohol, then charge the mixture with ammonia gas, cork the flask, and let it stand. Yellow crystals of ammonium thiocarbamate separate after a time, or can be obtained on evaporation.[2]

$$CS_2 + 2NH_3 = CS \begin{cases} NH_2 \\ SNH_4 \end{cases}$$
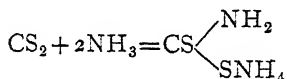
When this compound is decomposed by gentle heat, it does not directly afford thiourea, but gives ammonium isothiocyanate,[3] which latter, as we have

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[1] See Part II. p. 198.

[2] When CS_2 is dissolved in alcohol containing caustic potash in solution, *potassium xanthate* separates out in needles—

$$CS_2 + KOH + HOC_2H_5 = CS \begin{cases} OC_2H_5 \\ SK \end{cases} + H_2O.$$
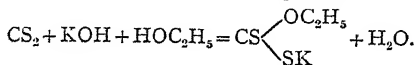
When an aqueous solution of the xanthate is added to copper sulphate, *yellow* copper xanthate precipitates ($\xi\alpha\nu\theta\delta\varsigma$ = yellow).

[3] This salt is easily prepared in quantity by a modification

already seen, requires a temperature above its melting-point for conversion into the metameric thiourea.

Ethyl thiocarbamate, or thiourethane, $CS\begin{cases} NH_2 \\ SC_2H_5 \end{cases}$
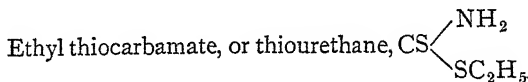
is known, but does not need special notice.

It has been already mentioned, at page 121, that sulphur analogues exist of cyanates and isocyanates of alcohol radicals. The following are the formulæ of the ethylic compounds :—

Normal	Iso-
$CN—O—C_2H_5$	$CO=N—C_2H_5$
$CN—S—C_2H_5$	$CS=N—C_2H_5$

We already know that the normal cyanate, when treated with ammonia, does not afford ethyl urea, whereas the iso-cyanate, or *ethyl carbimide*, does. Similarly the normal thiocyanate does not give ethyl thiourea when acted on by ammonia, but the iso-thiocyanate, or *ethyl thiocarbimide*, does.

The *normal thiocyanate* is easily obtained by dissolving potassium thiocyanate in absolute alcohol and heating with an equivalent of ethyl bromide ; potassium bromide separates out, and the liquid when distilled first gives the alcohol used as a solvent, and when the temperature rises to 140°, the nearly pure ethyl thiocyanate passes over as a colourless liquid of

of the above method. A mixture of carbon disulphide with 8 volumes of methylated spirit and 8 volumes of strong ammonia solution is allowed to stand for several days ; it is then distilled to a small bulk ; on cooling ammonium thiocyanate crystallises out.

sp. gr. 1·033. Nitric acid oxidises it to ethyl sulphonic acid : hence the structure assigned to it above.

Ethyl isothiocyanate, or ethyl thiocarbimide, is obtained in a wholly different way.

Experiment 749.—Add a few drops of carbon disulphide to an alcoholic solution of ethylamine,[1] and evaporate off the alcohol in the water-bath. Ethylamine acts as ammonia did in the last experiment, and affords a thiocarbamate, but containing ethyl, viz. :—

$$CS\begin{cases}NH(C_2H_5)\\SNH_3(C_2H_5)\end{cases}$$
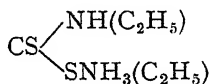
Dissolve the residue in water, and heat with solution of ferric chloride ;[2] the following reaction takes place :—

$$CS\begin{cases}NH(C_2H_5)\\SNH_3(C_2H_5)\end{cases} + Fe_2Cl_6 = CSN(C_2H_5) + 2FeCl_2$$
$$+ S + HCl + NH_3(C_2H_5)Cl.$$
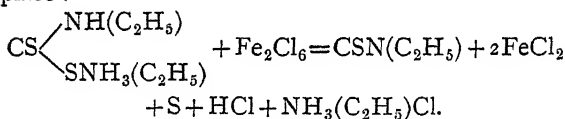
Ethyl thiocarbimide passes off in vapour with the steam, and the strong tear-exciting odour of *mustard* is noticed. All the thiocarbimides which contain alcohol radicals are characterised by this odour : hence Hofmann terms them all 'mustard oils.'[3] Ethyl

[1] Solution of methylamine may be more conveniently obtained, and can be used instead. Of course the methyl compound is then obtained.

[2] Mercuric chloride is generally recommended, but ferric chloride gives a better result.

[3] The volatile oil of black mustard is allyl thiocarbimide ; see p. 233.

mustard oil can be prepared in quantity as above ; it
is an oily liquid of sp. gr. 0·999, and boils at 134°.
Nitric acid withdraws ethylamine from it, while the
residue is oxidised to sulphuric and carbonic acids ;
the alcohol radical is therefore united to the *nitrogen*
of the mustard oil, and this, moreover, accords with
the mode of generation from a primary monamine.
Secondary and tertiary amines do *not* afford mustard
oils : hence the above reaction serves as a good test
for the primary bases.

When mixed with ammonia ethyl, thiocarbimide
quickly affords ethyl thiocarbamide, or ethyl thio-
urea—

$$CSN(C_2H_5)+NH_3=CS{\Large<}{NH(C_2H_5) \atop NH_2}$$
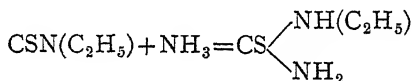
With ethylamine we can produce the diethyl thio-
carbamide.

Although urea is the chief product of tissue waste
in man, other nitrogenised bodies are met with in
urine ; for example, creatine, already noticed, and
uric acid, $C_5H_4N_4O_3$; the latter is the most important,
and is, moreover, related to urea : hence we shall next
examine it and some of its derivatives.

Experiment 750.—Acidulate about half a liter of
urine with two cubic centimeters of hydrochloric acid,
and allow it to stand in a warm place for a day. A
few dark-coloured brownish crystals separate ; these
consist of impure uric acid, and are to be collected on
a filter, washed well, and dried. To separate portions
apply the following treatment :—*a.* Heat in a test-

tube with a few drops of caustic potash ; the crystals dissolve as a soluble alkaline urate, $C_5H_2Na_2N_4O_3$, is formed. When the solution is acidulated with excess of hydrochloric acid, uric acid is displaced and re-precipitated as a light-coloured powder, insoluble in water and diluted acids. Uric acid[1] is dibasic.

b. Place the rest in a small porcelain dish, pour a few drops of strong nitric acid over it, and heat cautiously. The solid dissolves with effervescence. When the action is over, carefully evaporate nearly to dryness, pour a drop of ammonia on the residue, and heat again. A magnificent *purple red* colour is developed, termed *murexide.* This is a very delicate test for uric, or, as it is often termed, *lithic* acid.[2] This test will be explained later on (see p. 216).

In several of the lower animals nitrogen is chiefly excreted in the form of uric acid or urates ; thus ordinary *guano,* the dried excrement of sea-fowl, is rich in uric acid, and the solid *dejecta* of serpents chiefly consist of urates. The acid is easily prepared from good Peruvian guano by boiling the latter with caustic potash for some time in order to form soluble potassium urate, and acidulating the filtered liquid with hydrochloric acid. Two repetitions of the process generally suffice to remove colouring matter, and the acid is obtained as a white and inodorous powder.

[1] Uric acid exists in urine as an acid urate which is soluble at the temperature of the body, but, if excess be present, separates on cooling. It can be *redissolved* on warming the urine, and is thus easily distinguished.

[2] So called because one variety of calculus, or 'stone,' consists of the acid deposited from urine in the bladder.

When uric acid is heated with hydriodic acid in a pressure-tube, it affords *glycosine*, carbon dioxide, and ammonia; the two latter probably result from the decomposition of a *urea residue.* This observation suggested to Horbaczewski the synthesis of uric acid by heating glycosine with urea. He states that uric acid is obtained by carefully heating small quantities of pure glycosine (0·1 or 0·2 gm.) with fifteen parts of pure urea; the materials fuse, and uric acid slowly separates out. Three molecules of urea are concerned in this reaction, thus

$$\begin{array}{l}\underset{\text{Glycosine.}}{\underbrace{\begin{array}{l}\text{CH}_2\text{—NH}_2\\|\\\text{COOH}\end{array}}} + 3\text{CON}_2\text{H}_4 = \text{CO}\underset{\text{Uric acid.}}{\underbrace{\begin{array}{l}\diagup\text{NH—CO—CNH}\\\diagdown\text{NH—CO—CNH}\end{array}}}\\ \qquad\qquad + 3\text{NH}_3 + 2\text{H}_2\text{O}.\end{array}$$
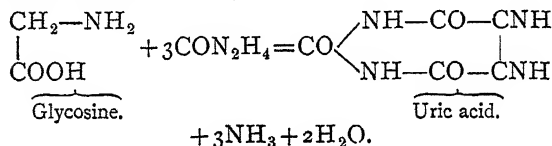
Uric acid may therefore be regarded as a urea derivative, or *ureide*, and most of the very numerous products it affords by (*a*) oxidation, or (*b*) reduction, may be regarded as ureides. We shall now briefly trace the relations existing between uric acid and its more important derivatives, first noting those obtained by *oxidation.*

Experiment 751.—Pour into a beaker about 10 c.cs. of colourless nitric acid of sp. gr. about 1·4, and add uric acid in small successive quantities. Each time that fresh powder is added, reddish fumes are evolved during solution; but when the latter no longer appear the addition of uric acid is to be stopped. On standing for a day or so, crystals separate, which are to be well drained from the acid liquid, and then dissolved in a small quantity of warm

water. Fine large crystals are obtained on cooling or evaporation, which consist of the compound $C_4H_2N_2O_24H_2O$ termed *alloxan*. This substance is a ureide of *mesoxalic acid*, which latter may be regarded as malonic acid (see p. 173) with two atoms of hydrogen replaced by one atom of oxygen. These relations are exhibited by the following formulæ:—

$$
\begin{array}{ccc}
\text{COOH} & \text{COOH} & \\
| & | & \text{NH—CO} \\
\text{CH}_2 \quad : & \text{CO} \quad : & \text{CO} \qquad \text{CO} \\
| & | & \text{NH—CO} \\
\text{COOH} & \text{COOH} & \\
\text{Malonic acid.} & \text{Mesoxalic acid.} & \text{Alloxan.}
\end{array}
$$
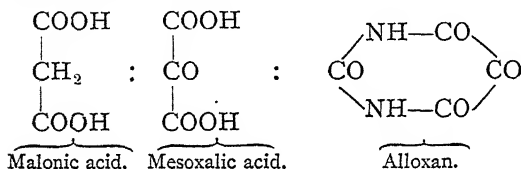
By continued boiling with baryta water alloxan ultimately affords mesoxalic acid and urea, or products of decomposition of the latter.

The acid liquid from which alloxan has crystallised contains a compound termed *alloxantine*, but the latter is more easily obtained by treating a solution of alloxan with hydrochloric solution of stannous chloride until the mixture becomes yellow; alloxantine is thrown down and can be collected, washed with water, in which it is very slightly soluble, and dried. Its composition is $C_8H_4N_4O_7$, and therefore contains one atom less of oxygen than two molecules of alloxan : hence it is a product of reduction of the latter. When heated with nitric acid it produces alloxan. Its constitution is probably

$$
\begin{array}{c}
\text{NH—CO} \qquad\qquad \text{CO—NH} \\
\text{CO} \qquad\qquad \text{C—O—C} \qquad\qquad \text{CO} \\
\text{NH—CO} \qquad\qquad \text{CO—NH}
\end{array}
$$
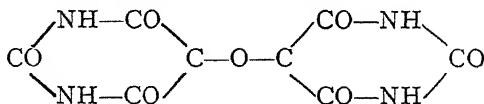
When alloxantine is treated with ammonia, two molecules of the latter combine and afford the beauful *murexide* obtained in testing for uric acid.

$$C_8H_4N_4O_7 + 2NH_3 = C_8H_4N_5O_6NH_4 + H_2O.$$

$\underbrace{}_{\text{Alloxantine.}} \qquad \underbrace{}_{\text{Murexide.}}$
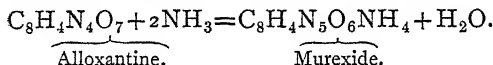
Murexide is the ammonium salt of an imide acid named *purpuric acid*. Potassium purpurate is formed by adding caustic potash to murexide : it is of a deep blue colour.

When uric acid is heated for a considerable time with strong nitric acid, the oxidation proceeds, and the ureide of *oxalic acid*, or *parabanic acid*, is produced, $C_3H_2N_2O_3$. When boiled with ammonia this compound is converted into the ammonium salt of *oxaluric acid*, $C_3H_4N_2O_4$, which is occasionally met with in urine. The relations of these compounds are evident from the formulæ—

$$CO\Big\langle{\substack{\text{NH—CO} \\ | \\ \text{NH—CO}}} \quad : \quad CO\Big\langle{\substack{\text{NH—CO—COOH} \\ \\ \text{NH}_2}}$$

$\underbrace{}_{\text{Parabanic acid.}} \qquad \underbrace{}_{\text{Oxaluric acid.}}$
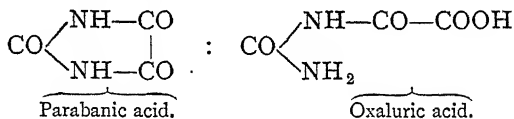
In the foregoing cases uric acid was oxidised by nitric acid, but if oxidised in neutral or alkaline liquids different products are obtained ; thus, when uric acid is boiled with water and lead peroxide is gradually added as long as it loses its brown colour, owing to formation of lead carbonate, the liquid affords crystals of the compound $C_4H_6N_4O_3$. This is termed *allantoin*, and is identical with the crystalline body obtained by Vauquelin from the allantoic liquor of

the cow. Grimaux has shown that it is the ureide of glyoxalic acid (see p. 158), having effected its synthesis by heating glyoxalic acid with two molecules of urea. Hence its structure is probably

$$CO \begin{cases} NH—CO—NH_2 \\ NH—CO—CHNH \end{cases}$$
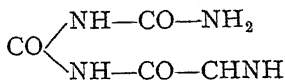
Numerous derivatives of allantoin have been obtained.

Uric acid admits of *reduction* in alkaline liquids; thus when treated with sodium amalgam it loses an atom of oxygen and is reduced to *xanthine*—

$$C_5H_4N_4O_3 + H_2$$
$$= C_5H_4N_4O_2 + H_2O.$$
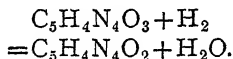
Xanthine is a crystalline powder which is very slightly soluble in water. When added to nitric acid, and the liquid evaporated, a *yellow* residue is left (hence its name), which is changed to a deeper yellow and then to red if heated with caustic potash. Xanthine occurs in minute quantity in urine, and has been met with as a calculus. A substance containing one atom less of oxygen than xanthine, and named in consequence *hypoxanthine*, or *sarcine*, is met with in the muscles of the heart and in some of the glands. *Guanine*, $C_5H_5N_5O$, is found in guano, and may be regarded as xanthine, in which one atom of oxygen is replaced by an imide (NH) group.

Xanthine, dissolved in caustic soda and treated with lead acetate, affords lead xanthine, $C_5H_2PbN_4O_2$. When that compound is heated with methyl iodide, dimethyl xanthine, $C_5H_2(CH_3)_2N_4O_2$, is obtained,

which is identical with the crystalline body *theobromine*, met with in chocolate prepared from *theobroma cacao*. Theobromine can in turn give the silver compound $C_5HAg(CH_3)_2N_4O_2$, which when heated with methyl iodide affords trimethyl xanthine, $C_5H(CH_3)_3N_4O_2$, a compound identical with the *caffeine* of coffee and tea.

Thus the crystalline bitter principles to which chocolate, coffee, and tea owe much of their useful properties are shown to be closely related to uric acid and derivable from it. Hence, by means of the synthetic operations we have indicated, caffeine can be manufactured from *guano*. The following table exhibits the relations of these remarkable compounds :—

Uric acid . . .	$C_5H_4N_4O_3$
. Xanthine . . .	$C_5H_4N_4O_2$
Theobromine .	$C_5H_2(CH_3)_2N_4O_2$
Caffeine . . .	$C_5H(CH_3)_3N_4O_2$

It may be added that the hydrogen replaced in all these cases appears to be *imidic* hydrogen.

CHAPTER LIX.

SAPONIFICATION — NATURAL FATS — SOAPS—GLYCE-
RINE — A TRIATOMIC ALCOHOL. GLYCERIDES—
MONO- AND DI-CHLORHYDRINES—TRICHLORIDE.
GLYCIDE—EPICHLORHYDRINE. GLYCERIC ACID—
PROPENYL, ALLYL—ALLYL IODIDE AND ALCOHOL.
ALLYL SULPHIDE—ALLYL MUSTARD OIL—MYRONIC
ACID—ALLYL THIOUREAS—SINNAMINE—PROPENYL
TRIBROMIDE— CARBALLYLIC ACID — ACROLEIN—
ACRYLIC ACID AND ITS HOMOLOGUES—PROTOGON
AND LECITHINE.

HAVING examined the monatomic and diatomic
alcohols related to hydrocarbides of the marsh gas
and ethylene series respectively, and their principal
derivatives, we have next to deal with the *triatomic*
alcohol, *glycerine*, referred to at page 48.

Glycerine is produced in the typical process of
saponification, i.e. true soap-making, in which animal
and vegetable fats are digested with caustic alkali.
Nearly all ordinary natural fats have been shown by
Chevreul to be esters, or mixtures of esters, of a single
triatomic alcohol radical, *glyceryl*,[1] C_3H_5'''. The

---

[1] Liebreich has lately shown that the fatty matter with
which wool is charged—*lanoleine*—and of which all fatty animal
exudation is said to chiefly consist, is an ester of the radical of

principal solid fat of palm-oil proved to be glyceryl tri-palmitate, or *palmitin* (which melts at 66°) ; that of mutton or beef suet is glyceryl stearate, or *stearin* (melting at 72°); while the oily body which can be expressed from lard and other natural fats is glyceryl oleate, or *olein*, which does not solidify at o°. These compounds are represented by the following formulæ :—

$$\left.\begin{array}{l} C_{15}H_{31}COO \\ C_{15}H_{31}COO \\ C_{15}H_{31}COO \end{array}\right\} C_3H_5 \quad : \quad \left.\begin{array}{l} C_{17}H_{35}COO \\ C_{17}H_{35}COO \\ C_{17}H_{35}COO \end{array}\right\} C_3H_5$$

$$\underbrace{}_{\text{Palmitin.}} \qquad\qquad \underbrace{}_{\text{Stearin.}}$$

$$: \quad \left.\begin{array}{l} C_{17}H_{33}COO \\ C_{17}H_{33}COO \\ C_{17}H_{33}COO \end{array}\right\} C_3H_5$$
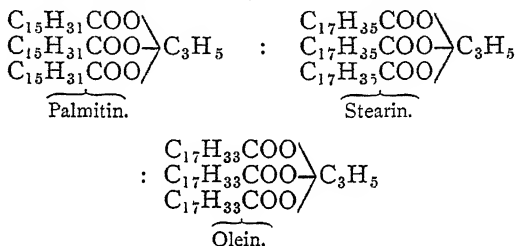
$$\underbrace{}_{\text{Olein.}}$$

On reference to the list of acids on page 81 it will be seen that the acid radicals of palmitin and stearin are members of the acetic series ; while that of olein contains two atoms less of hydrogen than the stearic radical, and, in fact, belongs to another series of acids, which will be presently referred to.[1]

Experiment 752.—Cut up some mutton or beef suet and throw the pieces into a little boiling water contained in a beaker ; the fat soon melts, and the liquid can be squeezed out from the animal membrane, the latter being removed and thrown away. The volume of water should not be more than

cholesterine, $C_{26}H_{43}OH$, a crystalline fat-like body of which *gall-stones* commonly consist. Cholesterine is a monatomic alcohol.

[1] See list of *acrylic* series of acids on p. 237.

four or five times that of the fat. Now add about
two volumes of strong caustic soda solution, and
digest in the water-bath with frequent stirring. Sapo-
nification gradually takes place, and the free fat
diminishes and then disappears after digestion for an
hour or longer, according to the quantities operated
upon. During this treatment the stearin is decom-
posed in the following way :—

$$\left.\begin{array}{l} C_{17}H_{35}COO \\ C_{17}H_{35}COO \\ C_{17}H_{35}COO \end{array}\right\} C_3H_5 + 3\,HONa$$

$$= 3(C_{17}H_{35}COONa) + \left.\begin{array}{l} HO \\ HO \\ HO \end{array}\right\} C_3H_5$$

$$\underbrace{\hspace{3cm}}_{\text{Sodium stearate.}} \qquad \underbrace{\hspace{2cm}}_{\text{Glycerine.}}$$
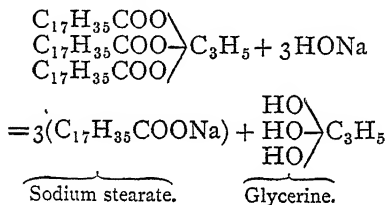
Now add to the soapy solution about half its volume
of a solution of *common salt*. A curd separates and
then melts and floats upon the mixture ; this is the
imperfect soap which has been thrown out of the solu-
tion by the common salt, in which ordinary soap is
insoluble. When cold remove the curd, wash it
slightly with water, and put into another beaker.
Most of the glycerine, $C_3H_5'''(OH)_3$, remains in the
brine, from which, however, it cannot be economically
separated. Add to the curd a little water and some
caustic soda solution, the latter in small quantity from
time to time until complete solution is effected, owing
to perfect saponification, then allow the liquid to cool,
when it becomes a more or less solid mass of *soap*.

Essentially the same process is carried out on the
large scale by prolonged boiling of fat with caustic soda

solutions of gradually increasing strength, and intermediate *curding* either by common salt or by strong alkaline liquids. The mass of soap finally obtained is cut into the usual 'bars' by wires.

Soaps produced with caustic soda are *hard*, i.e. they assume a firm consistence on partial drying; those made with caustic potash are *soft*, or jelly-like. Common *brown* soap contains more or less resin added in the later stages of saponification; the resin combines with the alkali and forms a kind of soap which mixes with that derived from the fat. Most common soaps contain much free alkali; those required for toilet use but little, and are prepared with great care. Transparent soaps are usually obtained from the finer varieties by solution in alcohol and evaporation of the liquid; the residue hardens on cooling. The celebrated Pears' soap may be taken as a good type of the best class of toilet soap.

· *Marine soap* is made by saponifying cocoa-nut oil. This soap is much more soluble in common salt solutions than the above, and consequently can be used for washing in sea-water.

Good white soap is soluble in diluted alcohol, and the solution is not precipitated by water; but if added to a solution of a calcium salt—the chloride for example—double decomposition takes place, and an insoluble lime soap is precipitated, thus, representing the acid radical of the soap by the symbol St—

$$CaCl_2 + 2(StONa) = CaSt_2 + 2NaCl_2.$$
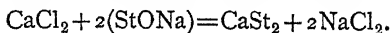
It is for this reason that water which contains much lime salts in solution is unsatisfactory for washing, as

enough soap must be used to precipitate all the lime before any detergent effect is obtained. Such water is said to be 'hard.'[1] Lead salts also precipitate soaps. When a solution of soap is treated with any acid, the soap is decomposed and the fat acid is set free. Should we desire to obtain glycerine rather than soap from a fat, it is necessary to use lead hydrate instead of the alkaline hydrate.

Experiment 753.—Place in a capsule about 100 grams of olive oil[2] (which consists largely of *olein*) and about three volumes of water, then heat on a water-bath, and stir in gradually 50 grams of finely powdered litharge (PbO), and continue to heat with frequent stirring for several hours until a pasty mass is obtained : this is *lead oleate*, or lead soap, the *emplastrum plumbi*, B.P.[3]

$$2[(C_{17}H_{33}COO)'_3C_3H_5'''] + Pb(OH)_2$$
$$= 3(C_{17}H_{33}COO)'_2Pb'' + 2[C_3H_5(OH)_3].$$
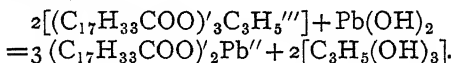
Pour off the water, which contains glycerine, dilute, and pass sulphuretted hydrogen to remove any lead in solution, filter, and evaporate on the water-bath. A sweet syrupy liquid is left, which is *glycerine*.

[1] A process for the determination of this 'hardness' of water is due to the late Dr. Clark, of Aberdeen, who used an alcoholic solution of soap for the purpose.

[2] It is well to mention at this point that olive, almond, and rape-seed oils do not dry up to a resinous mass on exposure to the air, whereas the oil expressed from *linseed* does resinify, especially after it has been boiled. The former are *non-drying*, the latter *drying* oils.

[3] When spread on linen, it forms common diachylon, or sticking-plaster. Lead oleate is distinguished from other and similar salts by its solubility in ether.

On the large scale glycerine is prepared by passing superheated steam through the molten fats, which latter undergo hydrolysis into glycerine and fat acids. These are carried along in the current of steam and are condensed with it, when the fat acids float on an aqueous solution of glycerine. The former are removed and used in soap and candle manufacture, while the glycerine is obtained from its filtered solution by simple evaporation.

Pure glycerine, $C_3H_5(OH)_3$, is a colourless, syrupy liquid. It owes its name to the fact that it has a sweetish taste. Its sp. gr. is 1·27; it boils at 290° with some decomposition. It does not mix with ether, but does readily with alcohol and water; the latter it even attracts from the atmosphere. It is an excellent solvent for a great variety of substances.

Experiment 754.—Suddenly heat a few drops in a capsule and note the acrid, tear-exciting smell produced. This is due to the production of *acrolein* (see p. 236) by dehydration, and constitutes a good *test* for glycerine. Glycerine acts as a triatomic alcohol; thus by heating with glacial acetic acid there are obtained in succession the following glyceryl acetates, often termed mono-, di-, and tri-*acetins*.[1]

$$
\begin{array}{c}
CH_3CO\!\!\diagdown \\
HO\!\!-\!\!\!\Big)C_3H_5 \\
HO\!\!\diagup
\end{array}
\quad : \quad
\begin{array}{c}
CH_3CO\!\!\diagdown \\
CH_3CO\!\!-\!\!\!\Big)C_3H_5 \\
HO\!\!\diagup
\end{array}
$$

$$
: \quad
\begin{array}{c}
CH_3CO\!\!\diagdown \\
CH_3CO\!\!-\!\!\!\Big)C_3H_5. \\
CH_3CO\!\!\diagup
\end{array}
$$

---
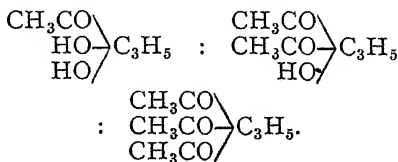
[1] The general term *glycerides* is often applied to all esters of the glyceryl radical.

Similarly stearines can be produced by the action of stearic acid. Nitric acid produces *nitrines* ; trinitrine, or *nitroglycerine*, is a dangerous and powerful explosive, and when mixed with a siliceous earth affords *dynamite*, which can be more safely handled than the trinitrine alone.

While the mode of obtaining glycerine, as well as the facts just stated, afford good evidence that it is a triatomic alcohol, the study of the action of hydrochloric acid and phosphorus chlorides on glycerine completes the proof of its constitution.

When glycerine is saturated with hydrochloric acid gas, the mixture requires to be heated on the water-bath for at least a week before one hydroxyl is replaced by chlorine and the following reaction realised :—

$$C_3H_5(OH)_3 + HCl = C_3H_5(OH)_2Cl + HCl.$$
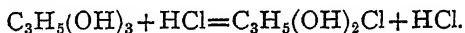
The product, a *monochlorhydrine*, when heated in a current of dry hydrogen to expel free hydrochloric acid, can be distilled at 213° with some decomposition, and is obtained as a liquid of sp. gr. 1·335, which easily mixes with water. Nascent hydrogen reduces it to the tricarbon *glycol*, $CH_3—CH(OH)—CH_2OH$.

Experiment 755.—Saturate a mixture of equal parts of glycerine and glacial acetic acid with hydrochloric acid gas, and then slowly heat until 130° is reached ; pour the residue into water. Somewhat impure *dichlorhydrine* is obtained as a heavy oil, which is slightly miscible with water ; it boils at 176°.

$$C_3H_5(OH)_3 + 2HCl = C_3H_5(OH)Cl_2 + 2H_2O.$$
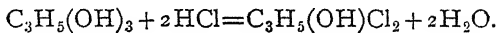
This is a liquid of sp. gr. 1·4. Nascent hydrogen reduces it to *secondary propyl alcohol*—

$$(CH_3)_2CH—OH.$$
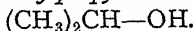
When dichlorhydrine is treated with phosphorus pentachloride, the last hydroxyl group is replaced, and the trichloride or *trichlorhydrine* $C_3H_5Cl_3$ is obtained.[1] It boils at 158°. Nascent hydrogen ultimately reduces it to *propane* C_3H_8.

The evidence, then, points to the following structure of glycerine[2] and the three chlorides :—

CH$_2$—OH	CH$_2$Cl	CH$_2$Cl	CH$_2$Cl
CHOH :	CHOH :	CHOH :	CHCl
CH$_2$—OH	CH$_2$OH	CH$_2$Cl	CH$_2$Cl.
Glycerine.	Monochlor-hydrine.	Dichlor-hydrine.	Trichloride.
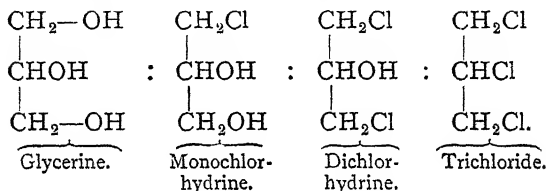
A metameric glycerine is theoretically possible, but it is unlikely to exist, as it would have two hydroxyl groups attached to one of the carbon atoms. The two metameric mono- and di-chlorhydrines—

CH$_2$OH	CH$_2$OH
CHCl :	CHCl
CH$_2$OH	CH$_2$Cl
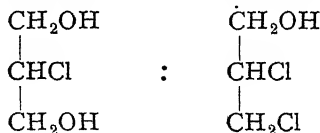
are known. The metameric dichlorhydrine is obviously *unsymmetrical.*

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[1] When these chlorides act on sodium ethylate, the OC$_2$H$_5$ group replaces the chlorine.

[2] Ony one higher glycerine is known, C$_4$H$_7$(OH)$_3$.

It follows from the foregoing that the structure of the *triad* hydrocarbide residue is CH_2—CH—CH_2. This radical is now generally termed *propenyl* rather than glyceryl. It will be remembered that when glycol chlorhydrine was treated with caustic potash ethylene oxide was produced (see page 145). When monochlorhydrine from glycerine is treated in the same way, a molecule of hydrochloric acid is also eliminated and *glycide* is obtained, which is an oxyhydrate—or part ether and part alcohol.

$$
\begin{array}{l}
CH_2Cl \\
| \\
CHOH \\
| \\
CH_2OH
\end{array}
+ _2KOH =
\begin{array}{l}
CH_2 \\
| \quad \rangle O \\
CH \\
| \\
CH_2OH
\end{array}
+ KCl + H_2O.
$$
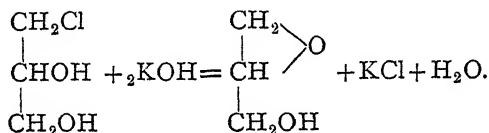
This is a liquid of sp. gr. 1·16. It boils at 162°. It easily assimilates a molecule of water and reforms glycerine. It can also react with glycerine itself and form polyglycerines. The true ether of glycerine is easily prepared by distilling pure glycerine with one-fifth of its weight of calcium chloride. Dehydration takes place, and the oxide is produced.

$$2(C_3H_5'''(OH)_3) = (C_3H_5''')_2O_3 + 3H_2O.$$
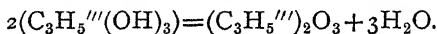
This ether is a liquid of sp. gr. 1·16, boiling at 171°. It recombines with water and forms glycerine.

When the symmetrical dichlorhydrine is treated with caustic potash, one molecule of hydrochloric acid is eliminated, and a body which is part oxide and part chloride, termed *epichlorhydrine,* is obtained.

$$\begin{array}{c} CH_2Cl \\ | \\ CHOH + KOH = \\ | \\ CH_2Cl \end{array} \quad \begin{array}{c} CH_2 \\ | \quad \diagdown \\ CH \quad \diagup O + KCl + H_2O. \\ | \\ CH_2Cl \end{array}$$
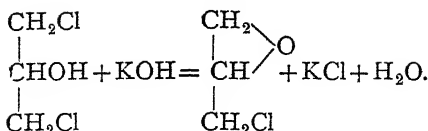
This is a liquid of sp. gr. 1·2, which boils at 117°. It is insoluble in cold water, but combines with it at 100°, and forms monochlorhydrine. It is metameric with monochloracetone. The trichloride, $C_3H_5Cl_3$, treated with water and caustic potash, affords glycerine.

The synthesis of glycerine from propylene, C_3H_6, has been effected by converting the hydrocarbide into propylene dichloride, $C_3H_6Cl_2$, and then into the tri-chloride, $C_3H_5Cl_3$, from which glycerine is obtained as above.

When glycerine is carefully oxidised by nitric acid, as in Experiment 727, *glyceric acid* is produced as a syrupy liquid; it is monobasic—

$$\begin{array}{c} CH_2OH \\ | \\ CH\ OH \quad + \ 2O = \\ | \\ CH_2OH \end{array} \quad \begin{array}{c} CH_2OH \\ | \\ CH\ OH + H_2O \\ | \\ COOH \end{array}$$
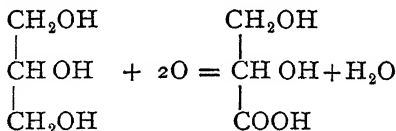
The acid is most easily precipitated as lead salt.[1]

By careful oxidation with potassium permanganate glycerine can afford a dibasic acid termed *tartronic* or oxymalonic acid, which latter can also be obtained by the action of hydrogen on mesoxalic acid. The

[1] When glyceric acid is heated strongly, it affords pyruvic acid (see page 185).

following formulæ make the relations of the three acids clear :—

CH₂OH		COOH		COOH

$$\begin{array}{ccccc} \text{CH}_2\text{OH} & & \text{COOH} & & \text{COOH} \\ | & & | & & | \\ \text{CHOH} & : & \text{CHOH} & : & \text{CO} \\ | & & | & & | \\ \text{COOH} & & \text{COOH} & & \text{COOH} \end{array}$$

<center>Glyceric acid.   Tartronic acid.   Mesoxalic acid.</center>
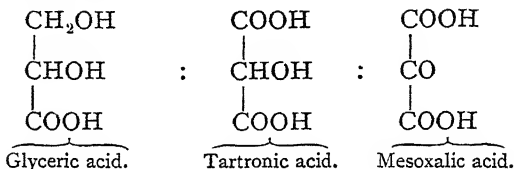
When glyceric acid is treated with hydriodic acid (phosphorus iodide), it affords the β form of iodo-propionic acid, while iodine is set free.

When glycerine itself is treated in a similar manner, it undergoes a remarkable change, and yields the iodide of the *monatomic* radical C_3H_5, named *allyl* because many of its compounds are met with in the *Alliums* or onion tribe.

Experiment 756.[1]—Heat some glycerine nearly to its boiling-point in order to render it anhydrous, then allow it to cool in a desiccator over sulphuric acid. Measure 16 c.cs. into a small tubulated retort, next add 14 grams of iodine in fine powder, and gently warm so as to get the iodine into solution, then cool down. Connect the retort with a condenser, and through the cork of the retort pass a glass tube delivering a slow current of carbon dioxide gas, with which the apparatus should now be filled, and kept filled through the experiment. Having cut up 5 grams of ordinary waxy phosphorus [2] in small pieces under

---

[1] This experiment is attended with some danger, and should only be undertaken under the close supervision of a teacher.

[2] If amorphous phosphorus were used for the same quantity of glycerine and double the weight of iodine, the *isopropyl*

water, dry a piece with bibulous paper, remove the
cork for a few seconds, and drop it into the retort. If
action does not take place after a short time, *very
gently* heat to start it ; when the active reaction is
over, add another piece of phosphorus, and so on.
Finally distil, add a little caustic potash to the distil-
late to remove free iodine, and draw off the layer of
heavy liquid and distil it again from calcium chloride,
as in the case of ethyl iodide. The product is *allyl
iodide*, C_3H_5I.

Pure allyl iodide is a colourless liquid, smelling
rather like garlic. Its sp. gr. is 1·79, and boiling-
point is 102°.

The change from the *triad* propenyl group to
monad allyl involves the double linkage of two carbon
atoms in the latter case—

$$
\begin{array}{ccc}
CH_2 & & CH_2 \\
| & & \| \\
CH & : & CH \\
| & & | \\
CH_2 & & CH_2 \\
\hline
\text{Propenyl.} & & \text{Allyl.}
\end{array}
$$
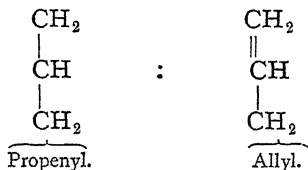
Allyl iodide is obviously an unsaturated sub-
stance, and can easily afford addition compounds ; for
example, when shaken up with mercury it produces
C_3H_5IHg. When this is heated it decomposes in the
following way :—

$$
\underbrace{2(C_3H_5IHg)}_{\text{Mercury allyl iodide.}} = \underbrace{(C_3H_5)_2}_{\text{Diallyl.}} + HgI_2 + Hg
$$
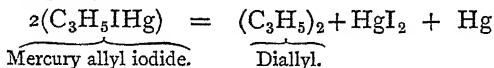
iodide, CH_3—CHI—CH_3, would be obtained. More or less of
this iodide is always formed in the production of allyl iodide
as above.

Allyl iodide can afford a hydrate or alcohol by the same line of treatment as that by which ethyl alcohol can be produced from ethyl iodide, or by simply heating with water. But Tollens and Henninger have made us acquainted with a much easier mode of preparing allyl alcohol directly from glycerine.

Experiment 757.—Into a retort of 300 c.cs. capacity, provided with a condenser, put 30 grams of ordinary oxalic acid and 100 c.cs. of glycerine. Pass a thermometer through the cork of the retort, and let the bulb dip well under the liquid. When the latter is heated to 130°, much carbon dioxide gas is evolved, and a little formic acid distils over ; continue to heat gradually up to 200°, when more carbon dioxide is evolved, and allyl alcohol comes over, which should be collected in a fresh receiver. It is useless to raise the temperature above 250°, as all the alcohol comes over below that point. The product is redistilled from another retort until two-thirds have passed over, and solid potassium carbonate is added to the distillate, which separates the alcohol as a light layer from most of the water that accompanies it. The alcohol is drawn off, allowed to stand for some time on solid potash, and then poured on fresh lime, from which it is finally distilled. The removal of the last traces of water is difficult. In this process it is probable that *propenyl monoformine* is first produced—

$$
\begin{array}{ccc}
\mathrm{CH_2-OH} & & \mathrm{CH_2-OCHO} \\
| & \mathrm{COOH} & | \\
\mathrm{CHOH} + & | & = \mathrm{CHOH} \qquad + \mathrm{H_2O} + \mathrm{CO_2} \\
| & \mathrm{COOH} & | \\
\mathrm{CH_2-OH} & & \mathrm{CH_2-OH.}
\end{array}
$$
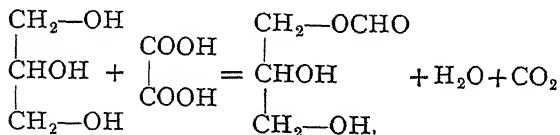
The formyl radical then acts as a reducing agent at a higher temperature, and allyl alcohol [1] results—

$$
\begin{array}{lll}
CH_2\!-\!OCHO & CH_2 & \\
| & \parallel & \\
CHOH & = \; CH & + \; H_2O + CO_2 \\
| & | & \\
CH_2OH & CH_2OH & \\
\underbrace{\hspace{3cm}} & \underbrace{\hspace{2.5cm}} & \\
\text{Monoformine.} & \text{Allyl alcohol.} &
\end{array}
$$
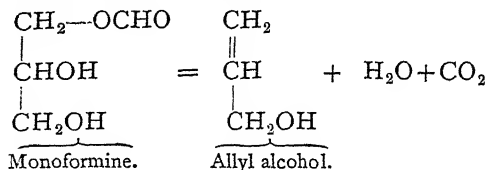
Pure allyl alcohol is a colourless liquid, having a very pungent smell. Its sp. gr. is 0·858, and its boiling-point 97°. It readily forms addition compounds owing to its unsaturated condition ; thus, it combines at ordinary temperatures with two atoms of bromine, and affords an oily dibromide, which is only slightly soluble in water ; the easy production of this compound serves for the separation of allyl alcohol. Allyl alcohol in many respects acts like ethyl alcohol, forming esters and allied compounds.

Allyl oxide, $(C_3H_5)_2O$, is obtained by acting with allyl iodide on sodium allylate, C_3H_5ONa, easily produced by dissolving sodium in the alcohol. It boils at 82°, and resembles *horse-radish* in smell.

The analogous sulphide, $(C_3H_5)_2S$, is obtained when allyl iodide acts on potassium sulphide. This is a liquid boiling at 140°, and is identical with the volatile *oil of garlic.*

The volatile oil of *black mustard* is also an allyl

---

[1] More or less allyl alcohol is produced in the preparation of formic acid as in Experiment 699. In that case also monoformine is doubtless first produced, and then breaks up at the lower temperature into formic acid and glycerine.

compound ; it is obtained by heating allyl iodide with potassium thiocyanate ; the product, which boils at 151°, is C_3H_5NCS, or 'mustard oil' *par excellence*. It is the isothiocyanate, or *allyl thiocarbimide*,[1] and possesses in a high degree the unpleasant smell and tear-exciting property of the other mustard oils described by Hofmann, and treated of in some detail at page 211, *et seq.* The oil does not exist ready formed in black mustard, but is developed when the powdered seed is mixed with water. The potassium salt of a complex acid termed by Bussy, who isolated it, *myronic acid*, is decomposed by a vegetable ferment, named myrosin, in presence of water, into mustard oil, glucose, and potassium acid sulphate, thus—

$$C_{10}H_{18}NKS_2O_{10} = C_3H_5—NCS$$

Potassium myronate. Mustard oil.

$$+ C_6H_{12}O_6 + KHSO_4.$$
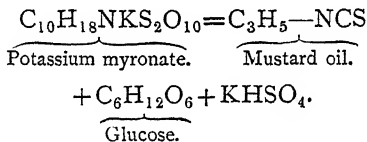
Glucose.

Consequently myronic acid is often referred to as a *glucoside.* When mustard oil is heated with diluted sulphuric acid, it affords allylamine and carbon oxysulphide.[2]

$$C_3H_5—NCS + H_2O = C_3H_5—NH_2 + CSO.$$
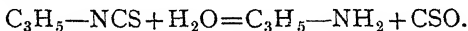
[1] The true thiocyanate, $C_3H_5—S—CN$, is known, and boils at 161°. It affords potassium thiocyanate when saponified ; the mustard oil does not when similarly treated.

Oil of mustard, as generally sold, contains more or less of the nitrile, $C_3H_5—CN$, or *crotonitrile*, which affords crotonic acid—$C_3H_5—COOH$ (see page 237).

[2] Carbon oxysulphide is also obtained on adding potassium

By treatment of allylamine with allyl iodide secondary and tertiary amines can be obtained analogous to the ethyl bases. Allylamine affords the mustard oil reaction with CS_2, &c. (see page 211). Allyl mustard oil affords *allyl thiocarbamide*, or *thiosinamine*, by shaking it up with excess of ammonia ; the oil gradually disappears, and the solution affords crystals of the allyl thiourea on evaporation—

$$C_3H_5-NCS + NH_3-CS\begin{cases} NHC_3H_5 \\ NH_2 \end{cases}$$
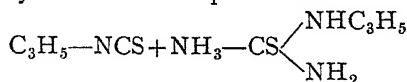
This is precisely analogous to the conversion of ethyl thiocarbimide into ethyl thiourea (see page 212).

Allyl thiourea affords allyl cyanamide or *sinamine* when desulphurised by heating with lead hydrate, just as the primary thiourea gives cyanamide on similar treatment.

While the radical allyl is thus seen to form compounds similar to those of ethyl or propyl, all the bodies into which it enters are found to exhibit the special tendency to form addition compounds, for the reason already stated, viz., the unsaturated condition of the radical. Advantage of this has been taken in the preparation of the propenyl derivative now to be mentioned from allyl iodide.

Experiment 758.—Heat allyl iodide with $1\frac{1}{2}$ times its weight of bromine. Iodine is displaced, and

thiocyanate to sulphuric acid, previously mixed with four-fifths of its volume of water, and cooled. The gas CSO is evolved without heat—

$$KNCS + H_2O + 2H_2SO_4 = CSO + NH_4HSO_4 + KHSO_4.$$
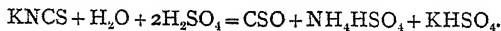
propenyl tribromide, $C_3H_5Br_3$, or 'tribromhydrin,' is obtained as a heavy oil, which crystallises at 16°, and boils at 220°.

Maxwell Simpson obtained the corresponding cyanide, $C_3H_5(CN)_3$, by heating an alcoholic solution of the bromide with potassium cyanide. When the propenyl tricyanide was then heated with caustic potash, the cyanogen groups underwent the usual conversion into carboxyl groups, and the potassium salt of *tricarballylic acid* resulted—

$$\begin{matrix} CH_2-CN \\ | \\ CH-CN \\ | \\ CH_2-CN \end{matrix} + 3HOK + 3H_2O = \begin{matrix} CH_2-COOK \\ | \\ CH-COOK \\ | \\ CH_2-COOK. \end{matrix} + 3NH_3$$
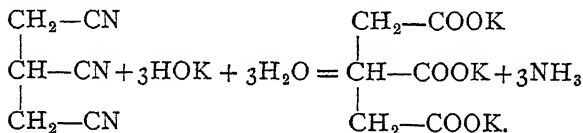
Tricarballylic acid is also obtained by heating citric acid with hydriodic acid; hence citric acid is oxytricarballylic acid (see page 188).

$$\begin{matrix} CH_2-COOH \\ | \\ C(OH)-COOH \\ | \\ CH_2-COOH \end{matrix} \quad : \quad \begin{matrix} CH_2-COOH \\ | \\ CH-COOH \\ | \\ CH_2-COOH \end{matrix}$$

$$\underbrace{\qquad\qquad}_{\text{Citric acid.}} \qquad \underbrace{\qquad\qquad}_{\text{Tricarballylic acid.}}$$
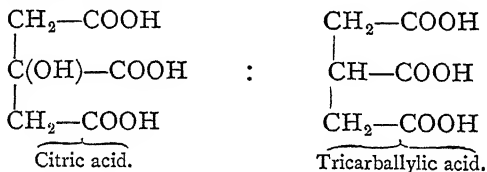
The analogy already pointed out between allyl and ethyl or propyl alcohols obviously suggests the existence of an aldehyde and an acid corresponding to those of the acetic series. These bodies are known, and are in fact most easily obtained from glycerine.

Experiment 759.—Mix glycerine with twice its weight of roughly powdered hydrogen potassium

sulphate in a retort, and heat the mixture by means
of an Argand gas-burner. An extremely irritating
vapour is evolved, identical with that obtained when
a few drops of glycerine or of olein are suddenly heated
in a capsule (see Exp. 754). This is the aldehyde
or *acrolein*, C_3H_4O, so named owing to its effect on
the nose and eyes. Its formation from glycerine is
represented by the equation—

$$
\begin{array}{ccc}
CH_2OH & & CH_2 \\
| & & \| \\
CHOH & = & CH \quad + 2H_2O. \\
| & & | \\
CH_2OH & & COH
\end{array}
$$
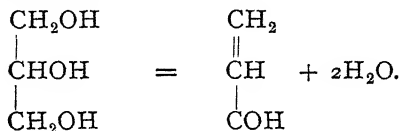
Acrolein boils at 52°; consequently the receiver must
be surrounded by a good freezing mixture in order to
secure its condensation. When a little is added to
ammonia-silver nitrate in a test-tube, and the mixture
is heated, the usual mirror of metallic silver is sepa-
rated on the sides of the tube as with other aldehydes.
It also affords Schiff's reaction. It unites with
ammonia, but *two* molecules react with one of
ammonia, and water is eliminated—

$$2C_3H_4O + NH_3 = C_6H_9ON + H_2O.$$
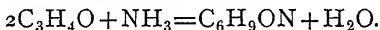
When exposed to the air, acrolein becomes acid and
passes into *acrylic* acid :—

$$
\begin{array}{ccc}
CH_2 & & CH_2 \\
\| & & \| \\
CH & +O= & CH \\
| & & | \\
COH & & COOH.
\end{array}
$$
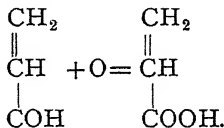
Acrylic acid is best obtained by shaking moist silver

oxide up with an aqueous solution of acrolein; the odour of the latter disappears after a time, while metallic silver and acrylic acid are obtained.

Acrylic acid is a liquid monobasic acid, and is unsaturated; hence it readily unites with bromine and forms dibromopropionic acid—

$$
\begin{array}{ccc}
CH_2 & & CH_2Br \\
\| & & | \\
CH & +2Br= & CH\ Br \\
| & & | \\
COOH & & COOH.
\end{array}
$$
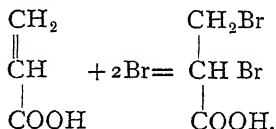
Acrylic acid is the first member of a group of acids, usually termed the *acrylic series*, each of which contains two atoms less of hydrogen than the corresponding acid of the acetic series, and all are unsaturated. The following are the most important :—

Acrylic acid	.	.	. C_2H_3—COOH
Crotonic „	.	.	. C_3H_5—COOH
Angelic „	.	.	. C_4H_7—COOH
Oleic „	.	.	. $C_{17}H_{33}$—COOH.

Crotonic acid is produced by the action of potash on allyl cyanide, or crotonitrile (see page 233) ; it was originally supposed to be present in croton oil, hence its name. *Angelic acid* is found in the free state in angelica root, and its esters are met with in cumin oil. *Oleic acid* is present in glyceryl ester in most of the liquid fats, and is separated by the method employed in Experiment 753, as the lead salt readily affords the free acid when heated with diluted sulphuric acid.

A very complex phosphorised compound termed

protogon has been separated from brain matter. Its composition is supposed to be represented by the expression $C_{160}H_{308}N_5PO_{35}$. It affords a glyceryl-phosphoric acid on decomposition, and therefore presumably contains the C_3H_5''' radical. Another complex phosphorised substance has been extracted from the yolk of eggs, and is consequently termed *lecithine*, $C_{42}H_{84}NPO_9$. It is a crystalline body which is a frequent constituent of growing animal and vegetable tissues.

CHAPTER LX.

HIGHER ALCOHOLS—ERYTHRITE, MANNITE—RELA-
TIONS WITH SUGAR GROUP—GLUCOSES—DEXTROSE
—SACCHARIC ACID—LÆVULOSE—CONSTITUTION OF
SUGARS—CANE-SUGAR OR SACCHAROSE—MANU-
FACTURE—INVERSION—RELATION TO GLUCOSE—
MALTOSE—LACTOSE, OR MILK SUGAR, &C.—STARCH
—CELLULOSE—PARCHMENT PAPER—PYROXILINE
—GUN-COTTON—COLLODION—GUMS.

BUT one tetratomic alcohol is definitely known, and that is a white, crystalline, and sweet substance named *erythrite*, $C_4H_6(OH)_4$, met with in very small quantity in several varieties of lichen and algæ, e.g. *protococcus vulgaris*, in which it occurs uncombined. This alcohol has been little studied as yet, but it is of theoretical interest, as tartaric acid appears to be simply related to it :—

$$
\begin{array}{ccc}
CH_2—OH & & COOH \\
| & & | \\
CHOH & & CHOH \\
| & : & | \\
CHOH & & CHOH \\
| & & | \\
CH_2—OH & & COOH. \\
\underbrace{\hphantom{CH_2—OH}} & & \underbrace{\hphantom{COOH.}} \\
\text{Erythrite.} & & \text{Tartaric acid.}
\end{array}
$$
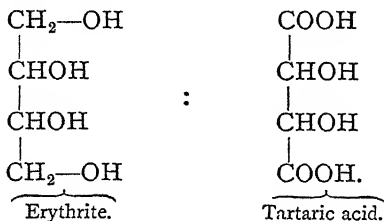
No well-marked pentatomic alcohol of the regular

series is known,[1] but a well-defined hexatomic alcohol can be easily prepared from common *manna*, which is the dried exudation of the Ash, *fraxinus ornus.*

Experiment 760.—Rub about 20 grams of manna with a little alcohol until a thin cream is formed, pour this into a flask, mix with 200 c cs. of strong methylated spirit, gradually heat to boiling, and keep it at that temperature for ten minutes or so, then quickly filter into a flask. The solution affords small crystals of *mannite*, $C_6H_8(OH)_6$. It is very sweet, as all the higher alcohols are, and easily dissolves in water, but not in ether.

Mannite undergoes a remarkable change when heated with strong hydriodic acid, as it gives hexyl iodide, thus—

$$\begin{array}{ll} CH_2OH & CH_3 \\ | & | \\ (CHOH)_4 + 11HI = & (CH_2)_4 + 10\,I + 6H_2O \\ | & | \\ CH_2OH & CH_2I. \end{array}$$
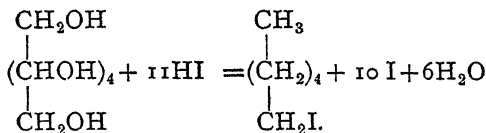
This reaction affords evidence of the presence of six hydroxyls in the compound. The chief interest about mannite is its close relationship to the *sugar* group, as it has been obtained by the action of nascent hydrogen on *grape sugar*, or glucose, $C_6H_{12}O_6$, and when oxidised it affords *saccharic acid*,[2]

---

[1] Quercite extracted from acorns, $C_6H_7(OH)_5$, possibly represents this group.

[2] A metamer of mannite termed *dulcite* is obtained from Madagascar manna. This affords on oxidation *mucic acid*, which is metameric with saccharic acid.

$C_4H_4(OH)_4(COOH)_2$, a body which is also obtained by the oxidation of glucose (see page 243).

We are thus led back to the *carbohydrates*, all of which contain C_6, or some multiple of C_6, in their molecules. Some of these we partially studied, as far as their general transformations were concerned, in the course of Chapter XLVII. We then learned that the compound *starch*, $C_6H_{10}O_5$,[1] when dissolved in water, and its solution boiled with a small quantity of sulphuric, afforded, first, *dextrine*, and then the variety of sugar termed *glucose*, $C_6H_{12}O_6$, the essential change being thus represented—

$$\underbrace{C_6'H_{10}O_5}_{\text{Starch.}} + H_2O = \underbrace{C_6H_{12}O_6}_{\text{Glucose.}}$$
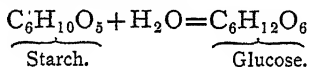
The solution of glucose obtained as in Experiment 671, if neutralised with chalk and evaporated to a small bulk, so as to allow any dissolved calcium sulphate to crystallise out, gives a sweetish, syrupy mother liquor which, when exposed in a desiccator over oil of vitriol, gradually affords a brownish mass, including nodular crystals. Gently warmed with strong alcohol, much of the sugar is dissolved and can then be obtained in nearly pure form by slow deposition from the alcoholic liquid.[2] It is less sweet than cane-sugar.

The aqueous solution of this glucose is *dextrorotatory* to polarised light ; it is therefore usually dis-

---

[1] This is given as the simplest expression for starch ; but that body is probably a high polymer of this (see p. 251).

[2] A solution containing one molecule of glucose and two of common salt affords crystals of a compound of the chloride with glucose.

tinguished as *dextrose.* Grape-sugar consists for the most part of dextrose, and this is present in many fruit juices. The sugar in the urine in *diabetes mellitus* is dextrose. We have already found that it reduces alkaline copper tartrate solution (see page 20)—one molecule reducing nearly five atoms of copper ; and that it is fermentable with yeast, affording ethyl alcohol [1] and carbon dioxide. It acts as a reducing agent with other oxides than copper, for example, with bismuth and silver.

Experiment 761.—To a solution of ammonia-silver nitrate add a little glucose or grape-sugar, and gently warm. Metallic silver slowly separates as a fine specular layer. Advantage of this property is taken in silvering the interior of glass vessels, and in producing silver reflecting surfaces for telescopes.

Experiment 762.—Dissolve a little glucose in water, add about half the volume of caustic soda, and heat. The liquid becomes more or less deep *brown* in colour. This is often called Moore's test, but is really due to Peligot, who asserts that a dark-coloured body, named by him *melassic acid*, is formed.

The most reliable of the tests for glucose is that with copper tartrate (Fehling's solution), described under Experiment 671. Glucose, when carefully oxidised with nitric acid, affords saccharic acid as well as more or less oxalic and other acids.

Experiment 763.—Pour about 10 c.cs. of nitric acid of sp. gr. 1·25 into a porcelain capsule, and add three grams of glucose ; gently warm until effervescence commences, then allow to cool down, and when

[1] And a little glycerine.

the mixture has acquired a brown colour place the capsule in as cool a place as possible. Crystals of oxalic acid separate, and the mother liquor, when poured off and allowed to evaporate at a low temperature in a thin layer on a large glass plate, gives some more oxalic and an acid gummy layer. The latter consists chiefly of *saccharic acid*, $C_4H_4(OH)_4(COOH)_2$. The ammonium salt of saccharic and mucic acids when strongly heated afford much *pyrrol*, C_4H_4NH (page 358).

When heated with acetic anhydride and acetic acid, glucose affords the compound $C_6H_7(C_2H_3O)_5O_6$, and with acetyl chloride $C_6H_7(C_2H_3O)_4ClO_6$, from which it appears that glucose contains only five atoms of hydrogen replaceable by acid radicals; hence, if an alcohol, it is *pentatomic*.

As already stated, glucose unites directly with hydrogen and affords mannite. When carefully heated with caustic alkali it gives, amongst other products, a *ketonic* alcohol *acetol*, $CH_3—CO—CH_2OH$,[1] and on oxidation by nitric acid, as we have just seen, it yields *saccharic acid*. It was supposed that glucose was an aldehyde of the alcohol mannite, because it was reduced to mannite by hydrogen, just as ordinary aldehyde is reduced to ethyl alcohol. Moreover, glucose reduces metallic oxides like aldehyde; but glucose does not afford Schiff's reaction, nor does it exhibit any of the other aldehydic properties. In addition, glucose gives acetol as above stated. These facts are more consistent with the view that glucose is

[1] When heated alone glucose and most of the sugars afford acetone itself.

a complex pentatomic ketonic alcohol than an alde-
hydic ; and the relations of mannite, glucose, and
saccharic acid may then be expressed by the following
formulæ :—

CH₂OH		CH₂OH		COOH
CHOH		CHOH		CHOH
CHOH	:	CHOH	:	CHOH
CHOH		CHOH		CHOH
CHOH		CO		CHOH
CH₂OH		CH₂OH		COOH
Mannite.		Glucose.		Saccharic acid.
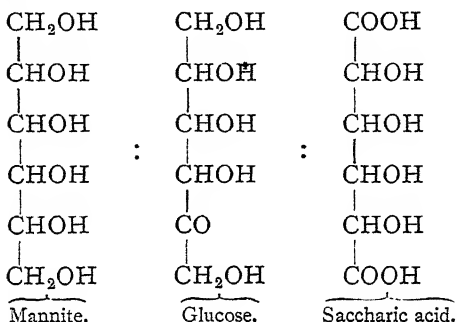
Another glucose, which has the same composition,
and appears to have the same structure as dextrose has,
but which is *lævorotatory*, is present in ripe fruits and
honey along with more or less dextrose.[1] It is named
lævulose, and can be separated from fruit sugar by dis-
solving it in water and adding to the solution calcium
hydrate in the proportion of half the weight of the sugar
used. The lævulose combines with the calcium hydrate
and forms a solid compound, whereas the dextrose
affords a soluble body.   The lævulose compound is
collected, squeezed, and diffused through water ; oxalic
acid solution is then very gradually added until a per-
sistent acid reaction is developed, the calcium oxalate
is filtered off and the filtrate evaporated, when the

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[1] It is probable that these bodies are physical isomers,
owing to the presence of asymmetrical carbon in the glucose
molecule.

lævulose is obtained as a gummy mass. Lævulose agrees in almost all particulars with dextrose, save in its action on polarised light and in the fact that it ferments much less easily than dextrose. A mixture of dextrose and lævulose is obtained by heating a solution of cane sugar (q.v.) with acids

Several other metameric glucoses are known, viz., galactose, arabinose, dambose, and inosite, but these do not require notice here. The last-named, *inosite,* is met with in human muscle, especially of the heart, and in some plants, but it is not optically active, and does not undergo ordinary fermentation.

The conventional type of sugars is the beautiful sweet compound derived from the sugar cane and from beetroot ; but it is a much more complex body than glucose, which is rather the *chemical* type of compounds of the class.

Cane-sugar or *saccharose,* $C_{12}H_{22}O_{11}$, as met with in the finest 'loaf-sugar,' is a crystalline substance very easily soluble in water. When its solution, which is dextrorotatory, is allowed to crystallise very slowly on immersed strings, beautiful monoclinic prisms are formed, as seen in 'sugar-candy.' It is slightly soluble in alcohol.

Experiment 764.—Heat a little white sugar in a capsule. It melts at 160°, or lower with a few drops of water, and can be cast in moulds wherein it solidifies to a transparent solid, or 'barley-sugar.' When the temperature is raised to 200°, a dark brown substance called 'caramel,' or 'burnt sugar,' is produced, which easily dissolves in water. The dark solution is used for various colouring purposes. Still

more strongly heated the purest form of *charcoal* is left.

Experiment 765.—To a small quantity of a strong solution of cane sugar contained in a large vessel add an equal volume of strong sulphuric acid. The mixture quickly colours, and a voluminous carbonised mass separates, while much steam and some sulphur dioxide are evolved.

. Cane sugar unites with several metallic oxides : thus with lime it forms a soluble compound, and advantage is sometimes taken of this fact to obtain a much stronger solution of lime than ordinary calcium hydrate solution, or 'lime-water.' With excess of lime it contains the compound $C_{12}H_{22}O_{11}(CaO)_2$.

Experiment 766.—Shake up in bottle 10 grams of slaked lime, 20 grams of cane sugar, and 200 c.cs. of water, let the mixture stand for a day, and then pour off the clear yellowish solution. This is the *liquor calcis saccharatus*, B.P., which contains about 4 per cent. of calcium hydrate, whose alkalinity is not interfered with by the sugar present.

Manufacture of Sugar.—Saccharose is present in many vegetable juices, but chiefly in that of the sugar cane and of common *beet*. The juice, extracted by pressure from sugar cane, is boiled to separate vegetable albumen, filtered and evaporated at as low a temperature as possible. Crystals of crude sugar separate, and a dark mother liquor, or *molasses*, is left ; this is sometimes fermented and produces 'rum.' When the crude sugar reaches the refiner, he dissolves it in water, filters the solution through animal charcoal to obtain a colourless syrup, and then boils the latter

down to the crystallising point in 'vacuum pans,' that is to say, in large copper boilers from which air is pumped out so that the liquid may boil at a much lower temperature than it would under ordinary atmospheric pressure. When a sugar solution is boiled at ordinary pressure, a considerable proportion of the sugar is converted into an uncrystallisable modification, whereas when boiled at lower pressure much less crystallisable sugar is lost in this way. A very concentrated syrup is run into conical moulds, and then nearly solidifies on cooling to a white crystalline mass, which, when drained from mother liquor and dried, constitutes 'loaf-sugar.' Less concentrated syrup is run into large cooling vats, where it is stirred to promote rapid crystallisation, and then transferred to centrifugal machines in which the syrup and sugar are rapidly separated, and the latter dried. This is ordinary 'soft sugar,' and the liquor is 'golden syrup.' When comparatively slow cooling is permitted, the beautiful small crystals of 'coffee sugar' are obtained.

Experiment 767.—Dissolve a little white cane-sugar in water and divide the solution in two parts.

Heat one part with copper tartrate solution, and note that reduction does *not* take place when the liquid is raised to the boiling-point, and only commences on prolonged boiling. Solution of cane-sugar is at once *distinguished* from one of glucose by this means.

Add to the second portion in a test-tube one-fifth of its volume of strong hydrochloric acid, and heat on the water-bath to about 60° for some time ; then

neutralise the free acid by caustic soda, add the copper solution, and heat ; reduction is now easily obtained, *as glucose is present.*

The change just noted is termed 'inversion,' and the substance in solution is 'inverted sugar,' which latter is a mixture in equal molecules of dextrose and lævulose. The latter has a higher rotatory power than dextrose, consequently the residual effect of the liquid is left-handed ; thus the right-handed solution of cane-sugar becomes left-handed by inversion. Further, cane-sugar solution does not directly ferment,[1] but inverted sugar ferments readily with yeast.

The inversion of cane-sugar involves the following change :—

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$
<div style="text-align:center">Cane sugar.   Dextrose.   Lævulose.</div>
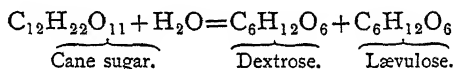
If we regard glucose as an alcohol, this union with the elements of water and production of two separate molecules of glucose points to cane-sugar as being a *diglucosic alcohol* analogous to diethylene glycol : thus—

$$
\begin{array}{ccc}
C_2H_4-OH & & C_6H_7O(OH)_4 \\
| & & | \\
O & : & O \\
| & & | \\
C_2H_4-OH & & C_6H_7O(OH)_4 \\
\text{Diethylene} & & \text{Diglucosic alcohol} \\
\text{glycol.} & & \text{(cane sugar).}
\end{array}
$$
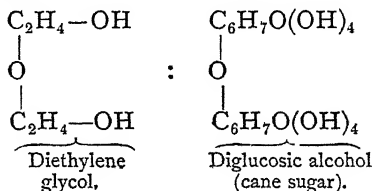
[1] In presence of active yeast, cane-sugar is slowly inverted, and then fermentation takes place.

A molecule of water can break each compound up into two separate alcohol molecules, in the one case of glycol, and in the other of glucose. Moreover, the presence of eight hydroxyl hydrogen atoms in cane-sugar has been shown by the production of an octo-acetate. As might be expected from the above constitution, cane-sugar affords much saccharic acid on oxidation.

It has been already pointed out that when the diastase present in malt solution acts on starch a variety of fermentable sugar is produced, which reduces copper, and is termed *maltose*. The nature of that body could not be considered at that stage of our enquiry, and it was thus treated as a glucose (which it does, in fact, produce in a fermenting liquor by further assimilation of water) in order to simplify the statement. But maltose has the same composition as cane-sugar, and is dextrorotatory; it appears to be formed along with dextrine by the hydration of starch—

$$3C_6H_{10}O_5 + H_2O = C_{12}H_{22}O_{11} + C_6H_{10}O_5.$$
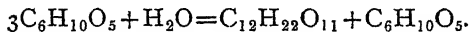
Another isomer of cane-sugar is the hard granular *lactose*, or 'sugar of milk,' obtained by the evaporation of whey. This is also dextrorotatory, and reduces copper solution.

A number of other sweet substances met with in plant juices are supposed to be metamers of cane-sugar. Thus the important group of sugars is divisible into two distinct classes : the GLUCOSES, which

are isomeric forms of the compound $C_6H_{12}O_6$; and the SACCHAROSES, which are isomers of $C_{12}H_{22}O_{11}$.

There is little doubt that the sugars are derived in nature from starch and its related bodies by processes of hydrolysis analogous to those we have already traced in Experiment 671, while the source of starch,[1] and of its isomer cellulose, is atmospheric carbon dioxide, as shown in the introductory chapter of this Part.

The separation of starch from grains and tubers, its chief characters, and its more important transformations into maltose, into *dextrine* (p. 19), and glucose (p 20), have been already sufficiently examined for the purposes of the present course, and the reader is referred to the portions of the text just quoted for those details. It is only necessary to point out here that the empirical formula $C_6H_{10}O_5$ for starch serves but to express the atomic ratios of its constituents as deduced from the best analyses of the purest attainable material, but its molecule probably includes many such groups, certainly not less than three, viz., $(C_6H_{10}O_5)_3$, or $C_{18}H_{30}O_{15}$; else it would be difficult to explain the production of maltose, $C_{12}H_{22}O_{11}$, and dextrine, $C_6H_{10}O_5$, from it under the influence of the diastatic ferment. Again, many regard dextrine itself as a much more complex body than the above formula would indicate, and recognise many polymeric or metameric modifications of it. It is assumed in con-

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[1] A starch-like or 'amyloid' body, termed *glycogen*, $C_6H_{10}O_5$, is separated from liver extract by the addition of acetic acid. This quickly passes into glucose, and is supposed to be the source of the sugar met with in the blood.

sequence that a much higher molecular weight must be assigned to starch than that which corresponds with the formula $C_{18}H_{30}O_{15}$. Thus Tollens concludes that the starch molecule is represented by $C_{30}H_{50}O_{25}$; O'Sullivan, to whose valuable researches this department of organic chemistry is largely indebted, gives $C_{72}H_{120}O_{60}$; while Messrs. Brown and Heron conclude that the most probable expression is $C_{120}H_{200}O_{100}$. It would not be desirable to discuss the evidence that can be adduced in support of these propositions at the present stage of the student's course; it is sufficient that he should understand that the starch molecule is probably a very complex one.

Similar remarks apply to *cellulose*, which is a polymer of $C_6H_{10}O_5$. Some of the properties of this body, however, require examination. The purest forms of cellulose for experimental purposes are cotton and pure white filtering paper—the latter is made by pulping cotton or linen tissues.

Experiment 768.—Dry a piece of thin white filtering paper, and plunge a part of it under the surface of some concentrated sulphuric acid, previously diluted with half its volume of water and cooled. The paper is not charred by this acid. After soaking for a few seconds remove the paper, wash it quickly first in plain water, and then in water containing a little ammonia. The paper is remarkably *toughened* by this treatment, and now resembles parchment in properties, though its composition is not altered. It is called parchment paper, and can be prepared in this way for use in dialysis (see Expt. 551, Part III.).

Experiment 769.—Introduce some more filtering paper into a portion of the same acid, and gently warm ; the paper softens after a time, and then gradually dissolves. If the solution be diluted and boiled for some time, glucose can be detected in the liquid, and the sugar could afford alcohol. The latter can in this way be manufactured from wood fibre and rags.

Cellulose dissolves in an ammoniacal solution of copper hydrate (Schweitzer's reagent), and much can be regained as an amorphous precipitate by the addition of excess of dilute acid.

The action of nitric acid on cellulose is specially interesting.

Experiment 770.—Mix in a beaker standing in a vessel of water 20 c.cs. of strong nitric acid and 20 c.cs. of strong sulphuric acid. Weigh out 4 grams of dry cotton wool, and, having torn it into small pieces, throw it into the acid and stir with a glass rod for three minutes, then drain away the acid quickly and throw the cotton into a large quantity of water ; it should then be thoroughly washed free from all acid in running water, squeezed, and allowed to dry in the air.

The product resembles ordinary cotton in appearance, but is more crisp when squeezed. When a small portion is brought near to a flame, it burns with a flash. Ordinary cotton is quite insoluble in a mixture of equal parts of alcohol and ether, but the specimen almost wholly dissolves, and a liquid is obtained which leaves on evaporation a nearly transparent skin, which is insoluble in water. This solution is the *collodion* used in surgery and in photography.

The substance dissolved is termed *pyroxiline*, B.P., and is a mixture of the two following compounds :—

Dinitrocellulose	. .	$C_6H_8(NO_2)_2O_5$
Trinitrocellulose	. .	$C_6H_7(NO_2)_3O_5$

When prepared in warm acids the trinitrocellulose is the chief product. This is the true explosive *gun cotton*, and is little dissolved by the mixture of ether and alcohol.

———————

Various trees afford transparent or translucent exudations, which are more or less soluble in water. These are termed *gums*, and are typified by the well-known *gum acacia*, or gum-arabic, used as an adhesive. Several of these bodies appear to be metamers of cane-sugar. They generally afford on oxidation *mucic acid* which is metameric with saccharic acid.

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The numerous *Glucosides* met with in nature appear to be esters of glucose, analogous to the acetyl compound mentioned on page 243.

CHAPTER LXI.

ACETYLENE—SYNTHESIS OF BENZENE—RELATIONS OF
   HYDROCARBIDES — AROMATIC COMPOUNDS — BEN-
   ZENE   FROM   COAL-TAR—MONOBROMOBENZENE—
   STRUCTURE OF BENZENE—ADDITION PRODUCTS—
   BENZENE METAMERS—DIPROPARGYL—RING FOR-
   MULA — NITROBENZENE, ITS PREPARATION AND
   PROPERTIES.

MOST of the compounds hitherto dealt with are
theoretically to be regarded as direct or indirect
derivatives of the paraffine, $C_nH_{2n\,2}$, series of hydro-
carbides, or of the ethylene, C_nH_{2n}, series.   In the
course of Experiment 261, however, we found that
the ethylene present in coal gas when burned with a
very limited supply of air, furnished the hydrocarbide
acetylene C_2H_2, which is obviously a member of
another series of unsaturated hydrocarbides of the
general formula C_nH_{2n-2}.

Acetylene is characterised by its property of
forming the red compound C_2H_2,Cu_2O when the gas
is shaken up with ammoniacal *cuprous* chloride.[1]   This
compound easily affords acetylene gas by mere addi-
tion of hydrochloric acid.

Acetylene is remarkable as being the only hydro-

[1] When dry it is explosive, but can be safely kept in a
somewhat moist state.

carbide formed when the electric arc discharge takes place between carbon poles enclosed in an atmosphere of hydrogen. This synthesis of acetylene was effected by Berthelot.

A very elegant mode of producing acetylene, which at the same time affords evidence of its constitution, is the following :—

Experiment 771.—Mix intimately two grams of iodoform, CHI_3, with three grams of zinc filings—or, better still, zinc powder ; introduce into a small flask provided with a delivery tube, and cover the mixture with a saturated solution of copper sulphate. The Gladstone copper-zinc couple formed attacks the iodoform, and, on gentle warming, gas is evolved which contains much acetylene, and when passed into ammoniacal cuprous chloride solution gives a good precipitate of the red copper acetylide. The change which affords the acetylene [1] may be represented as follows :—

$$\begin{matrix} CHI_3 \\ \\ CHI_3 \end{matrix} + 3Zn = \begin{matrix} CH \\ ||| \\ CH \end{matrix} + 3ZnI_2.$$
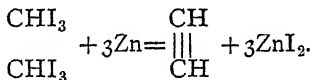
The triple linkage of the carbon atoms can be opened out in various ways—thus with bromine it affords

$$\begin{matrix} CHBr \\ || \\ CHBr \end{matrix} \quad \text{and} \quad \begin{matrix} CHBr_2 \\ | \\ CHBr_2 \end{matrix}$$
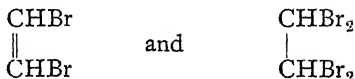
[1] A few of the higher homologues of acetylene are known, e.g. $CH \equiv C—CH_3$, or *allylene*. When the methyl group of this is oxidised to carboxyl, *propiolic acid*, $CH \equiv C—COOH$, results ; that body exists only in combination.

But a much more remarkable change occurs when acetylene is polymerised by heat and made to afford the hydrocarbide C_6H_6, or benzene. The following is Jungfleisch's method of demonstrating Berthelot's synthesis of benzene from acetylene.

Experiment 772.—Bend, as shown in fig. 157, a stout tube of hard glass, closed at one end. Fill it with mercury, and introduce about 20 c.cs. of acetylene liberated from the copper compound by hydrochloric

FIG. 158.
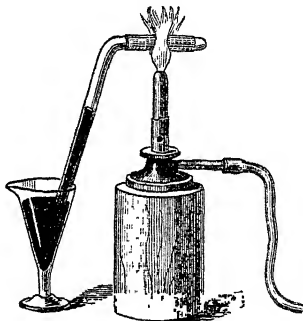
acid. Close the tube with a cork, but keep the latter under mercury. Wrap a portion of the tube as shown in copper gauze, and carefully heat the latter by means of the Bunsen flame. At a very low red heat white vapours appear in the tube and condense to a minute quantity of liquid, which increases on continuing the heat for ten or fifteen minutes. Then allow to cool down, and finally withdraw the cork under mercury ; the latter rises beyond its original level, proving the condensation of much of the ace-

tylene. The liquid *benzene*, C_6H_6, is the chief compound formed, and results from the union of three molecules of acetylene [1]—

$$3C_2H_2 = C_6H_6.$$
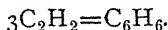
The theoretic interest of this synthesis is very great, and it directly raises the question of the constitution of benzene—a problem that must be kept clearly in view during all our operations with that body.

The vapour density of benzene accords with the expression C_6H_6 : hence the new compound is a member of a series of hydrocarbides of the general formula C_nH_{2n-6}, whereas the acetylene series is C_nH_{2n-2}. It follows from the law of declension in ratio of H : C, already noted in comparing one series with another, that an intermediate group of hydrocarbides should exist of the general formula C_nH_{2n-4}. Members of this group are known, and for the most part consist of *turpentines*, or terpenes, $C_{10}H_{16}$, a series of bodies whose consideration may be advantageously postponed until benzene and its derivatives have been studied. Up to this point, then, we can write out a list of hydrocarbide series as follows :—

Series.	General formula.	Example.
Paraffine	C_nH_{2n+2}	C_2H_6
Olefine	C_nH_{2n}	C_2H_4
Acetylene	C_nH_{2n-2}	C_2H_2
Terpene	C_nH_{2n-4}	$C_{10}H_{16}$
Benzene	C_nH_{2n-6}	C_6H_6

[1] When sufficient has been collected by a repetition of the operation, the benzene can be directly recognised.

The general term *Aromatic compounds* is applied to all substances which are derived from or related to benzene and its homologues, as these include most substances derived from plants and other sources, which possess strong aromatic odours.

Before commencing experiments with benzene it is necessary to obtain a better supply than the condensation of acetylene can afford; hence it is now desirable to state how the hydrocarbide is obtained in large quantity.

Benzene,[1] or benzole, was discovered in 1825 by the illustrious Faraday amongst the liquid products obtained by the compression of oil-gas; but it was found later on in large quantity mixed with the volatile hydrocarbides collected during the distillation of coal-tar (see Part II., Chapter XXI.). The product constitutes the 'light oil' of the tar distiller, because it floats on water, and is so distinguished from the less volatile liquids obtained during the process, which are heavier than water.

Benzene is separated from the light oil by a kind of fractional distillation, after successive washing, first with sulphuric acid to remove alkaline compounds, and then with caustic soda to withdraw acids. The most volatile liquids present are benzene, C_6H_6, which boils at $80.5°$, and a homologue of benzene named toluene, C_7H_8, which boils at $111°$. The vapours pass through a condenser surrounded by

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[1] Or benzol, the name given to the hydrocarbide, is due to the fact that it is most easily obtained in a state of purity by heating *calcium benzoate* (see page 314):

water, heated nearly to 100°; toluene condenses at this temperature, but benzene vapour passes on to a cold-water condenser, where it is obtained in the liquid form. Thus the two chief hydrocarbides of the oil are obtained in a sufficiently pure state for most purposes. By cooling the benzene thus separated to − 12°, beautiful leafy crystals of the pure compound form; when these are drained from the liquid and melted (they melt at 5·5°), the pure hyrocarbide is obtained. Such a product is now easily purchased, and is that which should be employed for experimental purposes.

Pure benzene, or *benzole*, is, at ordinary temperatures, a colourless, mobile liquid of peculiar odour. Its specific gravity is 0·885, and its boiling-point 80·5°. Its vapour is *very inflammable*, and burns with a smoky flame. The liquid is not soluble in water, but easily mixes with alcohol, ether, and chloroform. It is an excellent solvent for resins, oils, and fats.[1]

The chemical relations of benzene will appear in the course of experiments we shall follow.

The synthesis of benzene from three molecules of acetylene, $HC\equiv CH$, obviously could lead to the formation of a hydrocarbide somewhat similar in constitution to that of a six-carbon homologue of

[1] Another liquid is often sold for the removal of grease stains under the names of *benzoline* and *benzine collas* : these are the more volatile portions of paraffine oil, and do not contain benzene.

ethylene, C_6H_{12}, but including three doubly linked pairs of carbon atoms, thus—

C_6H_{12} . —CH_2—CH_2—CH_2—CH_2—CH_2—CH_2—
C_6H_6 . . . . —CH=CH—CH=CH—CH=CH—
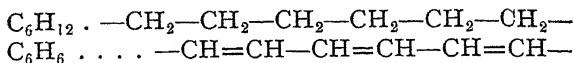
In that case it should be possible to add two atoms of bromine to benzene quite as easily as to the ethylene homologue. We shall now examine the action of bromine on benzene.

Experiment 773.—Into a flask of 100 c.cs. capacity pour 18 c.cs. of good benzene; next measure out 10 c.cs. of bromine near a good draught. These are in the proportions of nearly two atoms of bromine for one molecule of benzene. Plunge the bulb of the flask in cold water and gradually pour the bromine into the benzene. Note that *hydrobromic acid gas* is evolved; this points to displacement of hydrogen. When about half the bromine has been added, note that the mixture remains highly coloured by bromine; hence if an addition compound be formed, it is not produced as readily as with a member of the ethylene series. Then add the rest of the bromine and connect the flask by means of a rubber tube with a nearly upright condenser, so that condensed benzene or bromine may trickle back into the flask. From the top of the condenser must proceed a glass tube which should enter a vessel containing some water to condense hydrobromic acid gas. Now apply gentle heat to the flask; *much hydrobromic acid is evolved*[1] *as the*

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[1] A few drops of the water used to dissolve the gas will give an abundant precipitate of AgBr with silver nitrate.

brown colour of the liquid diminishes in intensity. When the acid fumes almost cease to come over, the process may be stopped.

The flask is now to be connected with a condenser in the usual position, and distilled from a water-bath. More hydrobromic acid is evolved, and some unchanged benzene distils, but a considerable proportion of brown liquid remains in the flask and does not distil at 100°. When cool pour this liquid into some water in which it will sink and not dissolve ; add some caustic soda to the water, and shake up to remove any free bromine. A colourless liquid is obtained, which, when separated from the water in the tube, fig. 153, and dried by standing on calcium chloride, distils for the most part at 155°, leaving a small crystalline residue in the flask.

The product is a liquid of sp. gr. 1·52, and is found on analysis to consist of C_6H_5Br. It is *Monobromobenzene.*[1] Therefore, as far as the action of bromine is concerned, it is certain that benzene is *not* analogous to an ethylene, because it does not afford a dibromide under conditions which easily determine the formation of an ethylene bromide. On the contrary, the experiment proves that *benzene acts as if it were a saturated hydrocarbide*, and in this respect it more nearly resembles a member of the marsh-gas series.

[1] Chlorine acts in a similar manner on benzene and affords *monochlorobenzene*, C_6H_5Cl. Iodobenzene, C_6H_5I, is obtained by the action of iodine in presence of iodic acid, which decomposes hydriodic acid as fast as it is produced by the attack on the hydrocarbide.

Notwithstanding this remarkable result, we know that six atoms of tetrad carbon, however joined together, are not likely to be really satisfied by six atoms of monad hydrogen, and hence that benzene must be capable of affording addition compounds if only we can realise the requisite conditions. It is found that the action of *sunlight* determines the formation of such addition compounds of benzene.

Experiment 774.—Support a tube containing a little of the hydrocarbide in a bottle of colourless glass, freely exposed to sunlight, and pour a good excess of bromine into the bottle, then cover the mouth of the latter with a glass plate ; combination takes place between the bromine vapour and that of benzene arising from the tube, and after several days' exposure a solid compound is obtained which consists chiefly of *benzene hexabromide*, $C_6H_6Br_6$. But it has not been found possible to form a more highly brominated compound from benzene without replacement of hydrogen.[1]

If benzene were an open chain of carbon atoms such as that represented by the expression on p. 260, it should not only have combined directly with bromine under the conditions of our experiment, but afforded an *octobromide*, $C_6H_6Br_8$. We now know that it does *not* give such a compound under any conditions, and therefore conclude that the six carbon atoms of benzene form a *closed chain or ring*—a structure capable of affording a hexabromide by addition, but not an octobromide. To the double

[1] When benzene is exposed to the action of an excess of chlorine in sunlight, the compound $C_6H_6Cl_6$ is formed.

linkage of three carbon atoms, required by this structure (as well as by the genesis of benzene from acetylene), is probably due the fact that the hydrocarbide acts as if it were saturated, and, under ordinary conditions, affords *substitution* rather than *addition* compounds, as we learned from Experiment 773.

It is interesting to note here that at least one open chain metamer of benzene is known in the compound *dipropargyl*, C_6H_6. That body is obtained in the following way :—Allyl iodide easily unites directly with an atom of mercury to form the compound C_3H_5IHg (see page 230). When this is heated, two molecules decompose thus—

$$2C_3H_5IHg = (C_3H_5)_2 + HgI_2 + Hg$$
$$\underbrace{}_{\text{Diallyl.}}$$
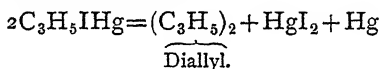
Diallyl easily combines with bromine, and yields a tetrabromide which affords *dipropargyl* by the continued action of caustic potash, four molecules of HBr [1] being eliminated ; thus

CH₂—CH=CH₂   CH₂C≡CH
| becomes |
CH₂—CH=CH₂   CH₂C≡CH [2]
     Diallyl.   Dipropargyl.
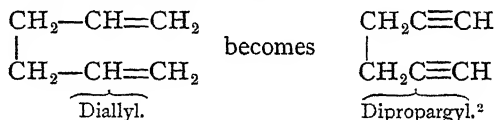
Dipropargyl combines very energetically with four

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[1] This actually takes place in two stages, the intermediate compound formed being *dibromodiallyl.*

[2] The acetylenic character of dipropargyl is shown by its formation of a compound with cuprous oxide. M. Henry states that he has recently obtained another open chain isomer of benzene which does not combine with cuprous oxide.

atoms of bromine in the first instance, and ultimately with eight, affording the compound $C_6H_6Br_8$.

The facts relating to benzene and its derivatives find their most satisfactory expression in what is termed the 'ring-formula' for that hydrocarbide, first proposed for it by Professor Kekulé of Bonn. The following represent benzene and monobromobenzene—

$$
\begin{array}{cc}
\text{CH} & \text{CBr} \\
\text{HC}\diagup\diagdown\text{CH} & \text{HC}\diagup\diagdown\text{CH} \\
\text{HC}\diagdown\diagup\text{CH} & \text{HC}\diagdown\diagup\text{CH} \\
\text{CH} & \text{CH}
\end{array}
$$
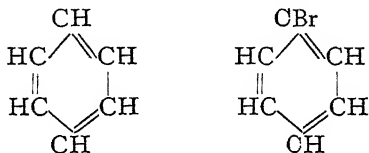
At present we shall only deal with mono-substitution derivatives analogous to the bromine compound, and need not use the ring expression, but the utility of the latter will appear when di-substitution compounds are considered in Chapter LXIII.

Monobromobenzene may obviously be regarded as the bromide of an apparently monad radical C_6H_5, which is termed *phenyl*.[1] Thus, according to this view, it is *phenyl bromide*, just as monobromethane is ethyl bromide. Unlike the latter, however, phenyl bromide holds its bromine so strongly that, when treated with silver oxide and water, no decomposition takes place ; therefore phenyl alcohol, C_6H_5OH,

[1] The free radical or *diphenyl*, $\begin{matrix} C_6H_5 \\ | \\ C_6H_5 \end{matrix}$ can be obtained by the action of sodium on two molecules of monobromobenzene.

cannot be obtained in that way, though it can be produced by other methods. See p. 277.

The action of nitric acid on benzene is quite as remarkable as that of bromine.

Experiment 775.—Pour into a Florence flask, supported in a beaker containing cold water, 20 c.cs. of benzene. Now add little by little, and with frequent agitation, a cold mixture of 40 c.cs. of strong nitric acid with 40 c.cs. oil of vitriol. Heat is developed, and oxides of nitrogen are evolved ; the external water prevents the temperature from rising too high, and the action becoming unduly energetic. At the end gently warm for a short time to about 60°, to complete the reaction, and when cold pour the whole into a considerable volume of water, with which the product should be well shaken up. A heavy reddish-yellow liquid, smelling strongly of bitter almonds, settles to the bottom of the water ; the latter is poured off, and the heavy oil is washed with more water, containing a little caustic soda, to remove free acid, and finally with plain water. The liquid is then separated from water by means of the funnel, fig. 153. It may be dried, and at the same time freed from unchanged benzene, by heating on the water-bath for a short time. The residue consists of nearly pure *nitrobenzene*, $C_6H_5NO_2$, which results from the reaction—

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O.$$
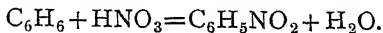
Nitrobenzene obtained as above is sufficiently pure for most purposes, but it distils at 207°, and is then obtained as a yellow, rather oily liquid of sp. gr. 1·207.

Though not miscible with water, nitrobenzene readily mixes with benzene, ether, and alcohol, and its solution in the latter solvent is often used for flavouring and perfuming soaps, under the name of *essence of mirbane*, instead of oil of bitter almonds. As nitrobenzene is poisonous, its use for such purposes is very dangerous.

CHAPTER LXII.

NITROBENZENE might obviously be regarded as *phenyl nitrite* if it were not for the fact that, unlike ethyl nitrite, it is not saponified by potash. It is, therefore, more probable that it is the analogue of nitroethane (see p. 43) rather than of the nitrite. If such be its constitution, it should give amido-benzene by reduction just as nitroethane affords amidoethane, or ethylamine, on similar treatment. This induction can be tested in the following way :—

Experiment 776.—Introduce into a 250 c. c. retort 50 or 60 grams of clean iron filings. On the latter pour about 10 c.cs. of nitrobenzene, and then, in small

successive portions, 20 c.cs. of strong acetic acid, and mix well. The acid generates hydrogen with the iron, but if the action becomes energetic, the retort should be cooled by external water. When all the acid has been added, cork the retort and place it on a water-bath with the beak nearly vertical, and digest for half an hour, or until all smell of nitrobenzene disappears. Then connect with a condenser, add 50 c.cs. of hot water to the contents of the retort, and distil rapidly. A turbid distillate is obtained, from which a nearly colourless oily liquid, of sp. gr. 1·026, separates, and can be drawn off in the usual way, dried by calcium chloride, and distilled alone. When pure it boils at 182°, though, as we have seen, it passes over with vapour of water at a much lower temperature. This compound is called *Aniline*, and its composition is $C_6H_5NH_2$. It evidently results from the reaction—

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O.$$
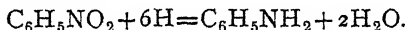
The production of this body settles the constitution of nitrobenzene; the latter is clearly analogous to nitroethane [1]—

$$C_2H_5\text{---}N\underset{O}{\overset{O}{\big<}} \quad : \quad \cdot C_6H_5\text{---}N\underset{O}{\overset{O}{\big<}}$$

Nitroethane.   Nitrobenzene.
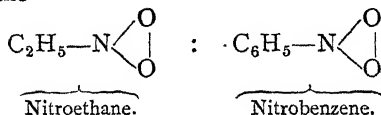
As the former gives amido-ethane or *ethylamine*

[1] A nitrite affords an alcohol with nascent hydrogen, and nitrogen is separated from the alcohol radical, ultimately appearing as ammonia.

on reduction, so nitrobenzene affords amidobenzene or *phenylamine* (aniline [1]) by reduction.

Aniline can be separated from the basic bodies distilled from coal-tar, but enormous quantities of it are manufactured by similar methods to that just followed, hydrochloric acid being now generally substituted for acetic acid, and other metals, capable of affording hydrogen by direct displacement, being used instead of iron. Ammonium sulphide can also be used to reduce nitrobenzene, but this method, usually termed ' Zinin's process,' is now seldom employed.

We have already seen (p. 119) that aniline easily affords phenylcarbamine, C_6H_5—NC, when heated with chloroform and caustic potash. This reaction, discovered by Hofmann, not only serves for the preparation of the carbamine, but proves that aniline is a primary *amine*.[2] However, it is not characteristic of aniline.

Experiment 777.—Pour a drop of aniline into half a test-tube of water, and add hydrochloric acid gradually to the mixture. Note that the aniline slowly disappears on shaking the liquid ; the solution then contains *aniline hydrochlorate*, or *phenylammonium chloride*, $C_6H_5NH_3Cl$, which could be obtained as a solid by evaporating the solution. Aniline unites with other acids to form analogous salts ; it affords in

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[1] Named *aniline* because first obtained by distillation of indigo—in Portuguese *anil*.

[2] Diphenylamine, $(C_6H_5)_2HN$, and triphenylamine, $(C_6H_5)_3N$, are also known. Moreover the residual hydrogen of aniline can be replaced by methyl, ethyl, &c., and *methyl-aniline*, $C_6H_5(CH_3)HN$, and dimethylaniline, $C_6H_5(CH_3)_2N$, obtained.

this way a nitrate, acetate, sulphate, and a less soluble oxalate.

Now add to the salt of aniline just produced a few drops of solution of 'bleaching lime,' and note that a beautiful *violet colour* is produced ; when the mixture is shaken up with ether, the latter rises to the surface coloured a fine blue.

Mr. W. H. Perkin was led by a knowledge of this reaction, and a similar effect which can be produced by chromic acid, to examine the products of the action of oxidising agents on crude aniline. He was rewarded by the discovery of the first of the magnificent 'aniline dyes,' and thus by the careful investigation of these apparently simple reactions he laid the foundation of a great branch of industry.

The beautiful *mauve* was the first of the dyes produced on the large scale, and was prepared by the action of bichromate of potassium on crude aniline sulphate containing the sulphate of a homologue of aniline, named toluidine (q. v.). Perkin has shown that the colouring matter includes the sulphate of a strong base derived from four molecules of amido compound, and named by him *mauveine* : to this body he assigns the formula $C_{27}H_{24}N_4$.

The red colouring matters are formed by heating aniline with certain oxidising agents, arsenic acid or nitrobenzene being used on the large scale, whilst for small experiments powdered mercuric nitrate is the most convenient ; a rich red or purple red tint is quickly developed, and the product can be at once dissolved in alcohol. The presence of toluidine is also essential to the production of the red colours

which result from three molecules of amido compound, and include the base *Rosaniline*, $C_{20}H_{19}N_3$. The detailed study of these bodies must be deferred to a later stage.

It is necessary to point out here, before proceeding with the examination of aniline, that the latter is by no means the sole product of reduction of nitrobenzene, and that intermediate compounds are known, some of which may be temporarily formed in the course of Experiment 776. When an alcoholic solution of nitrobenzene is treated with sodium amalgam (acidulating from time to time with acetic acid), the following compounds are formed in succession from two molecules of nitrobenzene :—

$$C_6H_5—N\diagdown \atop C_6H_5—N\diagup O \quad \text{and} \quad C_6H_5—N \atop \| \atop C_6H_5—N$$

Azoxybenzene.[1]   Azobenzene.
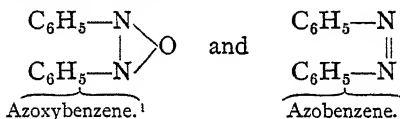
Azobenzene can take up two atoms of hydrogen, and then is formed symmetrical *diphenylhydrazine*,[2] $C_6H_5HN—NHC_6H_5$. Only two atoms more of hydrogen are required to split the hydrazine into two

[1] The prefix *azo* is derived from the French name for nitrogen, *azote*. Azoxybenzene is best prepared by boiling nitrobenzene with an equal weight of caustic potash dissolved in alcohol.

[2] When dissolved in hydrochloric acid, the hydrazine affords
$$C_6H_4—NH_2$$
its metamer *benzidine* $|$ which is precipitated from the
$$C_6H_4—NH_2$$
solution by ammonia.

molecules of aniline. These compounds melt at widely different temperatures.

Azoxybenzene, needle-like	crystals, fuse at		36°
Azobenzene, large red	,,	,,	67°
Diphenylhydrazine, tabular	,,	,,	131°.

When some salts of aniline are heated,[1] they lose water, and a phenyl-*amide* is obtained, as when ethyl ammonium acetate affords ethyl-acetamide. The bodies derived from aniline are termed *anilides*. The most interesting of them is *acetanilide* [2]—

$$C_6H_5—NH—CO—CH_3.$$
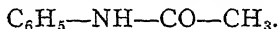
Experiment 778.—Mix equal volumes of aniline and glacial acetic acid in a flask connected with a vertical condenser, and gently boil for five or six hours. Then pour the product while warm and still liquid into a retort, and distil, using only a receiver. Acetic acid comes over first, and a liquid then distils, which solidifies in the neck of the retort, and is acet-anilide ; when this occurs change the receiver and continue the distillation, applying a Bunsen flame occasionally to the retort neck in order to liquefy the anilide and allow it to run into the receiver. It can be obtained pure by crystallisation from benzene. It melts at 112°, and boils at 295°.

$$C_6H_5—NH_3O—CO—CH_3=$$
$$C_6H_5—NH—CO—CH_3+H_2O.$$
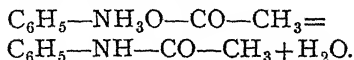
When acetanilide is heated with pentasulphide of

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[1] Aniline itself, when strongly heated in the state of vapour, affords an *imide* termed *carbazole*, $(C_6H_5)_2NH$.

[2] Used as a quinine substitute in medicine.

phosphorous *thiacetanilide*, C_6H_5—NH—CS—CH$_3$ is obtained.

As isocyanates and ureas are respectively imide and amide derivatives of carbonic acid, the phenyl compounds are anilidic as well.

Phenyl isocyanate, C_6H_5—N=CO, or *carbanile*, is obtained by the action of carbonyl chloride on melted aniline hydrochlorate. Like all the isocyanates it has a very pungent smell, and forms with ammonia phenyl urea, or *carbanilamide*—

$$C_6H_5\text{—NCO}+NH_3=CO\diagup^{NHC_6H_5}_{NH_2.}$$
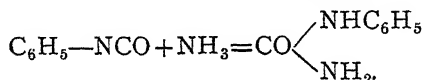
If instead of ammonia aniline be made to act on carbanile, symmetrical diphenyl urea, or *carbanilide*, is obtained—

$$C_6H_5\text{—NCO}+NH_2C_6H_5=CO\diagup^{NHC_6H_5}_{NHC_6H_5.}$$
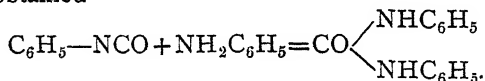
The related sulphur compounds are easily formed.

Experiment 779.—To a mixture of 10 c.cs. carbon disulphide and 20 c.cs. of absolute alcohol, contained in a flask provided with a vertical condenser, add 24 c.cs. of aniline, and heat for some hours over a water-bath. As in the case of acetanilide, a salt is first formed, in this case a phenylic thiocarbamate, on heating which sulphuretted hydrogen is evolved, and *thiocarbanilide* or diphenyl thiourea is produced—

$$CS\diagup^{NHC_6H_5}_{NHC_6H_5.}$$
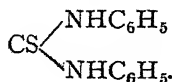
Evaporate the liquid on the water-bath, and shake up the crystals left with dilute hydrochloric acid, drain and crystallise from alcohol, in which the compound is easily soluble, though almost insoluble in water. It melts at 151°. This is the most convenient source of *thiocarbanile*, or phenyl mustard oil.

Experiment 780.—Boil a small quantity of thio-carbanilide in a test-tube with strong hydrochloric acid. The tear-exciting smell of the mustard oil is soon perceived, although sulphuretted hydrogen is evolved. The mustard oil boils at 220°. It is nearly insoluble in water, and separates out, while the solution contains the hydrochlorate of triphenyl-guanidine. The essential reaction is—

$$2CS\Big\langle{{NHC_6H_5}\atop{NHC_6H_5}} = C_6H_5{-}NCS$$

<center>Mustard oil.</center>

$$+C{=}NC_6H_5 \quad +H_2S.$$
$$\Big\langle{{NHC_6H_5}\atop{NHC_6H_5}}$$
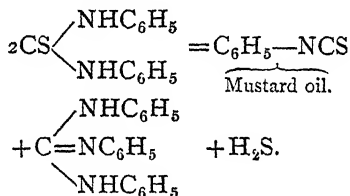
It is characteristic of primary amines of the fatty series that they should afford the corresponding alcohol when treated with *nitrous acid*. In this way ethylamine gives ethyl alcohol—

$$C_2H_5NH_2 + NO{-}OH = C_2H_5OH + N_2 + H_2O.$$
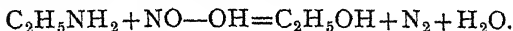
The question now arises whether phenylamine can yield phenyl alcohol when similarly treated. The following experiment supplies the answer :—

Experiment 781.—Convert about 5 c.cs. of aniline into its nitrate $C_6H_5{=}NH_3{-}NO_3$, by shaking with

it a mixture of 3 c.cs. strong nitric acid and 20 c.cs. of water. Drain the crystalline mass of nitrate from the acid liquid, put the purified compound into a flask, and add sufficient warm water to dissolve it completely. Now pass a current of the mixed oxides of nitrogen, generated as in Experiment 106, through the liquid. Much nitrogen gas is evolved as the solution warms, and a distinct smell of the well-known '*carbolic acid*' is perceived ; the odour becomes more marked on the addition of a little chalk to combine with the acids of nitrogen present.

Now the body called 'carbolic acid' bears the same relation to phenylamine that ethyl alcohol does to ethylamine, and its formula is C_6H_5OH. It is simply the hydrate of an alcohol radical, phenyl, and possesses the power of forming *alcoholates* analogous to sodium ethylate, but much more easily than the alcohols of the fatty series : hence it came to be regarded as an acid, though it is really an alcohol. The special name of *phenol*[1] is given to this alcohol, which is, moreover, the type of a class of alcohols containing benzene residues. The reaction in which aniline affords it is ultimately

$$C_6H_5NH_2 + NO—OH = C_6H_5—OH + N_2 + H_2O.$$
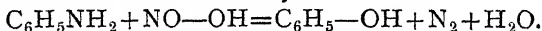
We shall presently examine phenol, but it is necessary to point out here that, just as in the case of reduction of nitrobenzene, we can recognise an intermediate stage in the conversion of aniline into phenol. If carefully cooled oxides of nitrogen are passed into a mixture of aniline nitrate with a little ice-cold water,

[1] Sometimes named *oxybenzene*, as its empirical formula is C_6H_6O.

and the temperature is never allowed to rise to 10°, the nitrate dissolves, and a mixture of ether and alcohol precipitates from the brown solution crystals of *diazo-benzene nitrate*, C_6H_5—N=N—NO$_3$.[1] This is an extremely unstable body which explodes with even a slight blow when dry. If its solution be boiled, it breaks up into phenol, nitrogen, and nitric acid, and it may have an ephemeral existence when the oxides of nitrogen act in the warm solution of aniline nitrate.

Diazobenzene chloride, C_6H_5—N=N—Cl, is formed when aniline hydrochlorate is mixed with sodium nitrite solution. By the action of tin and hydrochloric acid on the chloride, *phenylhydrazine* chlorhydrate is obtained—

$$C_6H_5—N=N—Cl + 4H = C_6H_5—HN—NH_2—HCl.$$
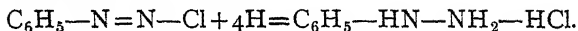
The hydrazine reacts with aldehydes, ketones, glucoses, and bodies containing the CO group, affording remarkably stable compounds. Thus with acetone it produces C_6H_5—HN—N=C(CH$_3$)$_2$, and water is eliminated. This is Fischer's hydrazine reaction.

Phenol can be prepared from benzene without the intermediate production of nitrobenzene and aniline.

Experiment 782.—Mix 20 c.cs. of benzene with the same volume of Nordhausen oil of vitriol in a

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[1] It is doubtful whether the hydrate of this base has been obtained. The nitrate added to alcoholic solution of aniline gives *diazo-amido-benzene*, C_6H_5—N=N—NHC$_6H_5$. The latter when heated in alcohol with aniline hydrochlorate gives the substance *amido-diazobenzene*, C_6H_5—N=N—C$_6H_4$—NH$_2$, which is a fine yellow dye.

flask fitted with a long tube to act as a condenser, or a vertical Liebig's condenser. Heat for a day on the water-bath with occasional agitation. The hydrocarbide gradually dissolves in the acid, water is eliminated, and *benzene-sulphonic acid* is formed—

$$C_6H_6 + H_2SO_4 = C_6H_5—SO_2—OH + H_2O.$$
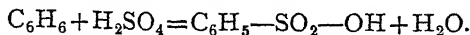
It is to be particularly noted that the new compound is a *sulphonic* and not a sulphovinic acid : in this respect again benzene acts as a saturated hydrochloride. Barium benzene-sulphonate is obtained in solution when the acid is treated with excess of barium carbonate and filtered ; but it is not necessary to do this when we desire to produce phenol : hence, neutralise the acid with caustic potash, then add as much more of the alkali, evaporate the whole to dryness in an iron dish, and fuse the residue at as low a temperature as possible, when the smell of phenol is easily perceived. Add a little water to the cooled residue, and then acidulate with hydrochloric acid ; if the liquid be warm, an oily layer of phenol separates. In this process—

$$C_6H_5SO_2OH + 2KOH = C_6H_5OH + K_2SO_3 + H_2O.$$
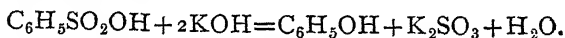
Phenol, or 'carbolic acid,' is now obtained in large quantities from coal-tar, in which it is present ready formed. The distillate from the tar that comes over between 160° and 200° is treated with caustic soda, which dissolves the phenol (as well as other similar bodies) ; the alkaline solution when separated and acidulated with an acid gives impure phenol as an oily layer, which is dried and distilled. The

fraction obtained between 170° and 190° is next placed in a freezing mixture, phenol crystallises out, and is then mechanically separated from the impure liquid.

Pure phenol, C_6H_5OH, is a colourless crystalline compound below 40° : at that temperature it fuses to a slightly yellowish or reddish liquid. It boils at 180°, and the odour of its vapour is very characteristic. It slowly dissolves in fifteen parts of water, and is easily miscible with alcohol, ether, benzene, and glycerine. It easily coagulates albumen, and acts energetically on the skin, soon whitening and destroying the cuticle. It is poisonous to man and the lower animals, and quickly arrests fermentation, apparently destroying the vitality of the organism concerned : hence it acts as a powerful *antiseptic*. It is easily dissolved by caustic soda, and the solution contains the compound C_6H_5ONa,[1] sodium phenolate, or 'carbolate,' which is easily decomposed even by atmospheric carbonic acid.

Experiment 783.—Shake up a little phenol with water. Note first that the solution is *not* acid, although the body forms the above-mentioned compound with caustic soda. Then add solution of ferric chloride to the liquid, when a fine *purple colour* is developed.[2]

Experiment 784.—Add a few drops of brominewater to aqueous solution of phenol ; a yellow precipitate is formed, even in very dilute solutions : this is tribromophenol, $C_6H_2Br_3OH$.

[1] The same body is formed when sodium is dissolved in phenol.

[2] Distinction from *creasote* of wood tar ; moreover, the latter does not gelatinise collodion as phenol does.

Experiment 785.—Dissolve some phenol in dilute ammonium hydrate solution, and add 'bleaching lime' solution ; note that a fine *blue*-coloured liquid is produced.

The foregoing serve as good *tests* for phenol or 'carbolic acid.'

In the second test we found that three atoms of bromine easily displace hydrogen in phenol, even in dilute aqueous solution, presumably in three distinct stages, though we cannot directly trace them in the process. Similarly the radical NO_2 can replace hydrogen in phenol, and afford *tri-nitrophenol*, or 'picric acid,' $C_6H_2(NO_2)_3OH$, by the action of strong nitric acid on phenol. As the action of the nitric acid on phenol often becomes very violent, and serious accidents have occurred during the preparation of picric acid, it is better for the student to purchase some and examine its properties. It occurs in yellow crystals, moderately soluble in water, and the solution has an intensely bitter taste. When added to a solution of potassium salt, a precipitate of $C_6H_2(NO_3)_3OK$ forms ; hence the compound is often used as a reagent of potassium in ordinary analysis. The precipitate when dried is explosive. It is remarkable that the presence of the NO_2 groups should render trinitrophenol comparable in acidic power with carboxylic acids.

A sulphur analogue of phenol, C_6H_5SH, is known and can be obtained by the reduction of benzene-sulphonic acid.

The general relations of phenol harmonise with the view that it is an alcohol. For example, when

treated with phosphorus pentachloride, phenyl chloride, C_6H_5Cl, is obtained. If with acetyl chloride, phenyl acetate is produced, which is analogous to ethyl acetate.

$$C_2H_3\text{—}O\text{—}C_2H_3O \qquad : \qquad C_6H_5\text{·}\text{—}O\text{—}C_2H_3O.$$

Again, the oxide of phenyl,[1] analogous to ethyl ether, exists—

$$\begin{array}{c}C_2H_5 \\ C_2H_5\end{array}\!\!\Big\rangle O \qquad : \qquad \begin{array}{c}C_6H_5 \\ C_6H_5\end{array}\!\!\Big\rangle O$$
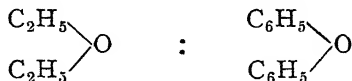
while mixed ethers can be formed by the action of methyl and ethyl iodides on the phenolates. In this way are produced

$$\begin{array}{c}C_6H_5 \\ CH_3\end{array}\!\!\Big\rangle O \qquad : \qquad \begin{array}{c}C_6H_5 \\ C_2H_5\end{array}\!\!\Big\rangle O$$

$$\underbrace{\qquad}_{\text{Anisol.}} \qquad\qquad \underbrace{\qquad}_{\text{Phenetol.}}$$

Lastly, salts of a phenylsulphuric acid, analogous to sulphovinic acid, are known—

$$\begin{array}{c}C_2H_5O \\ HO\end{array}\!\!\Big\rangle SO_2 \qquad : \qquad \begin{array}{c}C_6H_5O \\ HO\end{array}\!\!\Big\rangle SO_2.$$
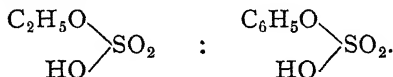
The acid is *not* formed when oil of vitriol acts on phenol, but phenol-*sulphonic acid* is produced instead ; its sodium salt is the *Sodii sulphocarbolas*, B.P.—

$$C_6H_5OH + SO_2\!\!\Big\langle{\begin{array}{c}OH \\ OH\end{array}} = SO_2\!\!\Big\langle{\begin{array}{c}C_6H_4OH. \\ OH\end{array}} + H_2O,$$
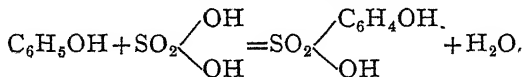
[1] The sulphide $(C_6H_5)_2S$ is also known.

It was long supposed that *phenyl-sulphuric acid* derivatives did not exist, but Baumann succeeded in separating its potassium salt from the urine of persons who had taken small doses of phenol, and then effected its synthesis by heating potassium phenylate with potassium anhydro-sulphate—

$$C_6H_5OK + KO-SO_2-O-SO_2-OK =$$
$$C_6H_5O-SO_2-OK + K_2SO_4.$$
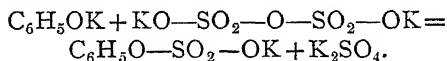
The evidence of the alcoholic character of phenol is therefore complete up to this point, but it does not afford an aldehyde nor acid, doubtless owing to the peculiar linkage of the carbon atoms in the benzene rings.

Just as ethyl alcohol affords metallic ethylates and ethides, so phenol gives *phenylates*, as we have already seen, and *phenylides*. The latter are obtained from bromobenzene by similar methods to those which suffice for the production of ethides from ethyl bromide. The only phenylide which is of much interest at present is the mercury compound, and this can be prepared in the following way :—

Experiment 786.—Mix in a flask containing a considerable volume of sodium amalgam, as in the Expt. 691 with mercuric ethide, 10 c.cs. of monobromobenzene, 2 c.cs. of ethyl acetate, and 10 c.cs. of benzene, or, better, of a coal-tar oil boiling about 130° ; connect the flask with an inverted condenser. After some hours' digestion, add 20 c.cs. of hot benzene, heat again, and filter the liquid from mercury and sodium bromide. The liquid on evaporation under a good draught affords small lustrous crystals of mer-

cury phenylide $(C_6H_5)_2Hg$. The reaction which occurs is similar to that which takes place in the formation of the ethyl compound.

Mercury phenylide melts at 120° and boils with decomposition at a much higher temperature. It is soluble in alcohol, but not in water. When its alcoholic solution is heated with mercuric chloride, it affords mercury chlorphenylide analogous to the chloroethide, viz. :—

$$Hg\!\!<\!\!\begin{array}{l} C_2H_5 \\ Cl \end{array} \qquad : \qquad Hg\!\!<\!\!\begin{array}{l} C_6H_5 \\ Cl. \end{array}$$
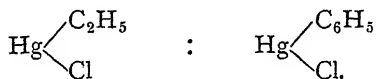
The positive radicals CH_3, C_3H_5, &c., can replace bromine or other halogen in benzene compounds just as the metals. This substitution was first effected by Fittig and Tollens. Their method consists in treating a mixture of monobromo- or monochloro-benzene, and the iodide, bromide, or chloride of the desired alcohol radical, with sodium. Thus monobromobenzene and methyl iodide can afford methyl benzene and sodium bromide and iodide.

$$C_6H_5Br + CH_3I + 2Na = C_6H_5CH_3 + NaBr + NaI.$$
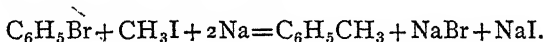
Similarly with ethyl iodide, and the higher homologues, various monosubstituted benzenes are obtainable.

Another and most effective method has recently been employed by Friedel and Crafts for the same purpose. They mix the hydrocarbide with the chloride of the alcohol radical, then introduce some aluminum chloride, which latter determines the

following change in some way not yet definitely understood :—

$$C_6H_6 + C_2H_5Cl = C_6H_5—C_2H_5 + HCl.$$
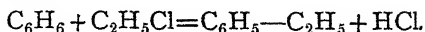
By such methods the following *monosubstituted* benzene homologues have been obtained :—

Benzene	C_6H_6
Methyl benzene . .	$C_6H_5CH_3$
Ethyl ,, . . .	$C_6H_5C_2H_5$
Propyl ,, . . .	$C_6H_5C_3H_7$
Butyl ,, . . .	$C_6H_5C_4H_9$
Amyl ,, , . .	$C_6H_5C_5H_{11}$
Hexyl ,, . . .	$C_6H_5C_6H_{13}$

Isomers of all the above substituted benzenes, with the exception of methyl-benzene, or *toluene*, are known, and some of them will be referred to in another chapter.

CHAPTER LXIII.

METAMERIC DIBROMOBENZENES—DINITROBENZENES—
  DIAMINES—NITRANILINES—DISULPHONIC ACIDS—
  DIPHENOLS—PYROCATECHINE, HYDROQUINONE,
  AND RESORCINE—QUINONE—ORCINE—DIMETHYL-
  BENZENES, XYLENES—PHTHALIC, TEREPHTHALIC,
  AND ISOPHTHALIC ACIDS—ORIENTATION OF ISO-
  MERS, DETERMINATION—HIGHER HOMOLOGUES
  OF BENZENE—MESITYLENE, &C.—TRIPHENOLS,
  PHLORGLUCOL, AND PYROGALLOL—MELLITIC ACID
  —PHENYLMETHANES—ROSANILINE.

IN the preceding chapters we have been almost
exclusively concerned with derivatives of benzene in
which only one hydrogen atom is replaced by other
radicals. We have now to proceed at least one stage
further in the formation of substitution products. In
doing so we shall follow the lines already laid down,
and avoid as far as possible the examination of
secondary changes, or similar details, which might
interfere with the perception of the general relations
of the somewhat complex substances arising from
benzene. It should be possible to replace another
hydrogen atom by bromine in monobromobenzene ;
hence we shall make—

Experiment 787.—Add 22 c.cs. of bromine to 40
c.cs. of monobromobenzene (or to 20 c.cs. of benzene),

and proceed as in Experiment 773, heating for two days, or until hydrobromic acid practically ceases to be evolved. Pour out the product into *hot* water, and carefully add caustic soda until the bromine is removed ; then pour off the water and let the heavy liquid cool, when crystals will separate. The crystalline mass, which is the chief product of the separation, is drained from a liquid, and is then dissolved in alcohol ; on evaporation of the solution crystals of *dibromobenzene*, $C_6H_4Br_2$, crystallise out. These melt at 89°. The liquid from which the crystals separated in the first instance, when carefully distilled, affords some monobromobenzene, which boils at 155°, and then a small quantity of a liquid which boils at 224° when pure. The latter does *not* afford crystals on cooling to the ordinary temperature, but its composition and molecular weight agree with the formula $C_6H_4Br_2$. It is therefore *metameric* with the first dibromide. A *third* dibromobenzene has been obtained by indirect means,[1] but it is not formed in the above experiment. It has not been found possible to produce more than three dibromobenzenes.

In summarising the chief characters of the three metamers as follows, it is convenient to distinguish them by the prefixes *o*, *p*, and *m*. Only the *o* and *p* compounds are formed in the direct attack of bromine and benzene :—

(*o*)	$C_6H_4Br_2$.	Liquid above 0° .	b.p. . .	224°
(*p*)	,, .	Crystals m.p. 89°	,, . .	218°
(*m*)	,, .	Liquid at −26°	,, . .	220°

[1] From a dibromaniline.

The remaining hydrogen atoms of benzene can be successively replaced by bromine until C_6Br_6 is reached.

Reasoning by analogy, we should expect nitro-benzene to afford dinitrobenzene by a continuation of the original treatment.

Experiment 788.—Mix in a flask about 10 c.cs. of the strongest nitric acid with the same volume of oil of vitriol, and to the warm mixture add very gradually 20 c.cs. of nitrobenzene. When the first action is over, heat the liquid, gently at first, and then to boiling for a few minutes. Allow the contents of the flask to cool somewhat, and then pour out slowly into about two liters of water ; the now solid product is to be thoroughly washed with fresh water, drained and dissolved in boiling alcohol, and crystallised. The first crop of crystals consist of a nearly pure *dinitro-benzene*, $C_6H_4(NO_2)_2$, which fuses at 90°. The mother liquid when carefully evaporated affords a metamer which melts at 171°, and on boiling off the rest of the alcohol, a *third* dinitrobenzene is obtained which melts at 118°, but no more than three such bodies are known. We shall distinguish the dinitro-benzenes in the same way as the dibromo- compounds—

(*o*) $C_6H_4(NO_2)_2$.	Needle-like crystals .	m.p.	171°
(*p*) ,, .	,, .		118°
(*m*) ,, .	,, .		90°

The *m* product is the one obtained in largest quantity.

The reduction of the above dinitrobenzenes by iron and acetic acid, as in the preparation of aniline (Experiment 776), affords *three* corresponding metameric *diamidobenzenes*, $C_6H_4(NH_2)_2$. These bodies are *diamines*, analogous to ethylene diamine (p. 148), and have been named in consequence *phenylene-diamines*. Their chief characters are contrasted below; but it may be added that only *three* metamers are known and all are crystalline compounds—

(*o*)	$C_6H_4(NH_2)_2$	—	m.p.	102°	b.p.	252°
(*p*)	,,	—	,,	140°	,,	267°
(*m*)	,,	—	,,	63°	,,	287°[1]

If a dinitrobenzene be reduced with ammonium sulphide (Zinin's method referred to in the last chapter), but one of the NO_2 groups is attacked, and a *nitraniline*, or nitroamidobenzene, $C_6H_4{<}^{NO_2}_{NH_2}$ is obtained. *Three* metameric nitranilines are known.

Similarly three metameric disulphonic acids, $C_6H_4(SO_2OH)_2$, are known, *o*, *p*, and *m* varieties, and three corresponding *iodo-phenols*, $C_6H_4INO_2$, are obtainable by the action of a mixture of iodine and iodic acid on ordinary phenol.

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[1] This particular phenylene diamine is an exceedingly delicate reagent for *nitrous acid*. When its solution is added to a nitrite and dilute hydrochloric acid, a fine *yellow* colour is quickly developed; this is due to the formation of *triamido-azobenzene*, $\begin{matrix} N—C_6H_4NH_2 \\ \| \\ N—C_6H_3(NH_2)_2 \end{matrix}$ which is a fine yellow-brown dye, known as 'Bismarck brown.'

Fusion of the disulphonic acids with potash, or boiling of the iodophenols with the same alkali, enables us to produce three metameric *dihydroxy-benzenes*,[1] which are diatomic alcohols analogous in some respects to the glycols. These diatomic phenols are obtained from other sources that we must shortly refer to, as each phenol bears a special name which connects it with one of those particular sources. The compounds are all crystalline—

(o) $C_6H_4(OH)_2$ *Pyrocatechine* . . m.p. 104° b.p. 245°
(p)   ,,   *Hydroquinone* . ,, 169° ,, 250°
(m)   ,,   *Resorcine* . . . . ,, 110° ,, 270°

Pyrocatechine, or *catechol*, is obtained by dry distillation of catechu. It is also a common product of the action of heat on astringent principles of plants. It has been met with in the red autumn leaves of the Virginian creeper, and has been recognised in morbid urine, in one instance by Dr. Walter Smith.

A solution of pyrocatechine affords a deep green colour with ferric chloride, and the liquid becomes deep red on addition of an alkali.

Hydroquinone, or *Quinol*, was identified by Wöhler as a product of the reduction by sulphurous acid of *quinone*, $C_6H_4O_2$. The latter is produced in many processes of oxidation of disubstituted benzenes, but it can also be obtained from aniline by careful oxidation of the latter with three times its weight of potassium bichromate in about 20 volumes of dilute (1 : 2) sulphuric acid. After standing for twenty-four hours,

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[1] Sometimes termed dioxybenzenes, because the empirical formula is $C_6H_6O_2$.

much quinone is formed, and is extracted when the liquid is shaken up with ether. If now the solution be evaporated, quinone separates in brilliant golden-coloured needles, which melt at 116° and readily sublime. Its vapour is very pungent and tear-exciting. Sulphurous acid first produces green *quinhydrone*—

$$C_6H_4 \left\langle \begin{array}{l} OH \\ O \end{array} \right.$$
$$|$$
$$C_6H_4 \left\langle \begin{array}{l} O \\ OH \end{array} \right.$$
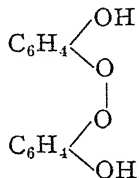
and then by further reduction two molecules of hydroquinone result. In this and other reactions quinone acts like a peroxide, but it also combines with hydroxylamine and produces a *quinoxime* like a ketone. With ferric chloride hydroquinone is oxidised, at first to green quinhydrone and then to yellow quinone.

Resorcine, or *resorcinol*, is obtained when several oleo resins and gum resins, *assafœtida, galbanum,* &c., are heated with caustic alkali. It owes its name in part to that circumstance, and partly to the fact that it is a lower homologue of another diatomic phenol, named *orcine*,[1] $C_6H_3(CH_3)(OH)_2$, which has been extracted from certain lichens, archil, litmus, &c.

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[1] When its alcoholic solution is mixed with ammonia and exposed to the air, oxygen is absorbed and a magnificent violet-red liquid is obtained which contains *orceine*.

Resorcine solution gives a fine *violet* colour with ferric chloride.[1]

Again, three metameric dimethylbenzenes can be obtained by applying Fittig and Tollens's reaction (see p. 282) to each of the dibromobenzenes, and the following liquids result :—

(*o*) $C_6H_4(CH_3)_2$. Liquid . b.p. 140°
(*p*)   ,,   .   ,,   . ,, 137°
(*m*)   ,,   .   ,,   . ,, 137°

These liquids are generally termed *xylenes*, and are met with in coal-tar oils. These xylenes and higher methylated benzenes will be referred to in some detail further on (see p. 297).

Lastly, the three xylenes, or dimethylbenzenes, when oxidised by potassium permanganate in presence of alkali, afford three corresponding acids, or dicarboxylbenzenes, which also have the special names given below :—

(*o*) $C_6H_4(COOH)_2$. Phthalic acid. Melts about 190°, and gives anhydride.

(*p*) $C_6H_4(COOH)_2$. Terephthalic. Sublimes unchanged.

(*m*) $C_6H_4(COOH)_2$. Isophthalic. Sublimes unchanged.

Phthalic acid is also formed by heating naphthalene (or better, nitronaphthalene, see Chap. LXV.) for

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[1] It is well to note that resorcine is more stable at high temperatures than the other two phenols, and is often formed at high temperatures from the same materials that afford hydroquinone when less strongly heated.

a long time with nitric acid. It is obtained in fine crystals, which are easily soluble in hot water and but slightly when cold, and also dissolve in alcohol and ether. When heated, the acid melts, and very easily splits up into water and the anhydride, which boils at 277° and solidifies in fine crystals—

$$C_6H_4(COOH)_2 = C_6H_4\left\langle\begin{array}{c}CO\\CO\end{array}\right\rangle O + H_2O$$

$\underbrace{\hphantom{C_6H_4(COOH)_2}}_{\text{Phthalic acid.}}$ $\underbrace{\hphantom{C_6H_4\langle CO \ CO\rangle O}}_{\text{Phthalic anhydride.}}$
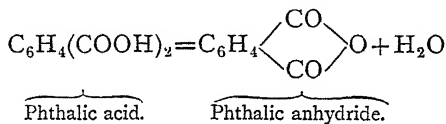
Experiment 789.—Heat a small quantity of the anhydride with its own weight of sulphuric acid and twice its weight of phenol to 120° for an hour, next pour into water and wash the resinous mass obtained. Then dissolve in spirit; note that it affords a solution which, when treated with a little ammonia, produces a magnificent red colour. The compound that reacts in this way is *phenol-phthalein*, $C_6H_4(CO - C_6H_4OH)_2$. Resorcine [1] and other phenols give similar compounds, some of which afford beautiful colours with alkalies.

Terephthalic acid is produced by the action of dilute nitric acid on turpentine. It is a white powder, very slightly soluble in water, hot or cold, and insoluble in alcohol. It sublimes unchanged, and does *not* afford an anhydride on heating.

Isophthalic acid is obtained by the long-continued

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[1] This compound exhibits a beautiful green fluorescence, and is termed *fluorescine*. Its easy production serves as a good test for resorcine on one hand, or phthalic acid or anhydride on the other.

heating of *m* xylene with chromic acid or alkaline permanganate ; it occurs in fine colourless needle-like crystals. It is somewhat soluble in boiling water, and separates out on cooling. It dissolves in alcohol also. Like the last acid it sublimes without affording an anhydride.

All the acids form soluble salts with ammonia ; when these solutions are tested with barium nitrate, barium phthalate or terephthalate is precipitated, but the isophthalate is not thrown down, as it is a very soluble salt. By means of all the foregoing characters the three acids admit of clear distinction. All three when strongly heated with lime break up into benzene and carbon dioxide—

$$C_6H_4(COOH)_2 = C_6H_6 + 2CO_2.$$
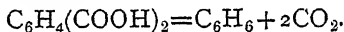
To sum up, then, we have recognised the following facts :—

(1) That no true metamers of *monosubstituted* benzenes are known. It may be added that all attempts to produce them have failed.

(2) That *three* metamers of each *disubstituted* benzene are known, and *three only*.

These are pure matters of fact, apart from any hypothesis. But we can readily found on them the following conclusions, independently of those to which we have been already led, as to the structure of benzene itself. From (1) we conclude that each of the six hydrogen atoms of benzene is united in the same way to carbon,[1] and consequently that all have

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[1] Ladenberg is disposed to restrict this statement to four out of the six, but on grounds that seem to be insufficient.

the same value in chemical exchange, just as in the simpler case of marsh gas. From (2) that, in disubstituted compounds, the two replacing radicals can only differ *in position* in each of the three metameric molecules, since (*a*) the hydrogen atoms of benzene are of equal value, and (*b*) all question of possible internal grouping of replacing radicals is excluded in dealing with the three dibromo- or dichloro-benzenes, in which the elementary atoms of the halogens replace those of hydrogen.

Thus, the stress of facts obliges us to recognise a new kind of isomerism, or, more correctly, metamerism, *that of position.*

Kekulé's ring, or hexagon, formula for benzene enables us to picture to our minds the possible relations of the three metameric disubstituted benzenes.[1] Let us take the case of the dibromobenzenes, and compare them as below with monobromobenzene as the starting point for disubstitution :—

$$C_6H_5Br \qquad oC_6H_4Br_2 \qquad mC_6H_4Br_2 \qquad pC_6H_4Br_2$$

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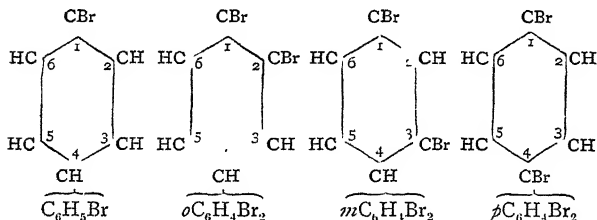
[1] Ladenberg represents the carbon atoms of benzene in such a way as to form a *prism* rather than a ring, while Claus has proposed another figure. Kekulé's ring formula is more simple than either, and suffices for the explanation of the facts.

In these diagrams [1] the positions are numbered, for convenience of reference, in the direction the hands of a watch move, and we assume that in monobromobenzene the carbon atom marked ' 1 ' is that whose hydrogen has been replaced by Br. The substitution of a second atom of H by Br can then obviously occur at any of five other points, but only *three* of these can be regarded as distinct positions.

In the *o* (or *ortho*) position above (1 : 2) the hydrogen of adjacent carbon atoms is replaced by Br ; then, in the *m* (or *meta*) position (1 : 3), *one* CH group intervenes ; while in the *p* (or *para*) position (1 : 4) *two* CH groups connect those whose H has been replaced by Br. It is obvious, however, that the relative positions 1 : 5 and 1 : 3 are the same, and 1 : 6 and 1 : 2 are also identical ; hence, not more than *three* distinct positions can be recognised, and no more than three metameric disubstituted benzenes are possible. As we have seen, groups of three *only* are known.

Thus, the ' position theory ' accords with the facts, and serves to explain complex phenomena which are inexplicable in any other way at present known to us. It has, moreover, admirably served the great purpose of every hypothesis—that of stimulating and assisting the further investigation of nature.

In future, we shall refer to the members of metameric groups as *ortho-*, *meta-*, or *para-* compounds when the replacent occurs in the positions 1 : 2, 1 : 3, or 1 : 4 respectively. It may be added that, in the lists

[1] The double linkage of carbon is not shown above, as it may be set aside in the consideration of substituted benzenes.

of metameric compounds given in the early part of this chapter, the *o*, *p*, and *m* compounds are the ortho-, para-, and meta- derivatives. Thus, the *orientation* (as it is termed) of the isomeric bodies has been already indicated.

The student will naturally inquire at this point how the extent of the orientation can be determined—in other words, how we can ascertain whether a dibromobenzene is an ortho-, meta-, or para- compound. Practically, such a problem is often one of much difficulty, but the *principle* involved in its solution can be shortly indicated. Several solutions are possible, but the most reliable one is that given below, which is due to Körner, a distinguished pupil of Professor Kekulé.

The dibromobenzenes, when acted on by another molecule of bromine, exchange a third hydrogen atom for bromine, and afford in each case at least one *tribromobenzene*, $C_6H_3Br_3$. Knowing this, and postulating the equivalence in chemical exchange of the hydrogen atoms in benzene, reference to the diagram on p. 293 will show that the *number* of tribromobenzenes possible depends on the relative positions of the two bromine atoms already present in the compound under examination. It is obvious that in orthodibromobenzene, *i.e.* the 1 : 2 compound, only *two* really distinct positions remain, viz. 1 : 3 and 1 : 4 ; therefore, the *ortho*-dibromide can only afford *two* triderivatives. In paradibromobenzene, *i.e.* the 1 : 4 compound, only *one*, the meta, or 1 : 3 position, remains ; hence, a *para*-dibromobenzene can only give *one* triderivative.

Lastly, metadibromobenzene can obviously afford *three* triderivatives, since the third bromine atom can replace hydrogen in the positions 2, 4, or 5, in the latter case producing a *symmetrical* tribromobenzene.[1] Thus, the orientation is determined by observing the maximum number of distinct triderivatives that can be produced. Other replacing radicals can be used for this purpose, and are often more convenient in practice, but the principle involved is the same.

Having determined the orientation of the dibromobenzenes, the latter can be converted into the corresponding dimethylbenzenes, or xylenes, by Fittig and Tollens's reaction (see p. 282); in this way the orthodibromobenzene can be converted into orthodimethylbenzene, and so on; thus, the orientation of the xylenes can be indirectly ascertained. This result obviously admits of being checked in turn by the formation of trisubstituted xylenes, the number of the latter obtainable serving independently to determine the orientation of the xylene examined. Again, the xylenes can be oxidised to the phthalic acids (see p. 299); thus, orthoxylene affords phthalic acid (orthophthalic), paraxylene gives terephthalic acid (paraphthalic), and metaxylene yields isophthalic acid (metaphthalic). The general principle is therefore far-reaching in its application.

Lastly, if methyl, ethyl, &c., replace hydrogen in benzene, these carbon groups are termed *side chains.* When but one side chain occurs, as in the list of

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[1] The student will find it convenient to follow this statement by drawing benzene rings on paper, and marking off the positions indicated above,

hydrocarbides on p. 283, no metameric bodies are possible ; but when *two* side chains are present, as in dimethylbenzene, and in similar disubstituted benzenes containing the higher homologues of methyl or analogous radicals, it is possible to determine the orientation by oxidation, for it has been found that, however long the two side chains of carbon compounds may be, each one is ultimately decomposed and oxidised to a single carboxyl, and the compound finally affords one of the phthalic acids. It is, therefore, only necessary to ascertain which of the phthalic acids results from the complete oxidation of the side chains in order to determine the orientation of the original compound. On reference to p. 290 it will be seen that the characters of the three phthalic acids are strongly marked, and their recognition therefore comparatively easy.

By successive replacement of the hydrogen of benzene by methyl groups the series of hydrocarbides in the following list have been obtained from the primary benzene :—

Benzene	.	.	.	C_6H_6	
Toluene	.	.	.	$C_6H_5(CH_3)$	$= C_7H_8$
Xylene	.	.	.	$C_6H_4(CH_3)_2$	$= C_8H_{10}$
Cumene	.	.	.	$C_6H_4(CH_3)_3$	$= C_9H_{12}$
Durene	.	.	.	$C_6H_2(CH_3)_4$	$= C_{10}H_{14}$
Pentamethylbenzene	.			$C_6H(CH_3)_5$	$= C_{11}H_{16}$
Hexamethylbenzene	.			$C_6(CH_3)_6$	$= C_{12}H_{18}$

Metameric modifications of mono-, penta-, and hexa-*methyl* benzenes are not known to exist, but we

have already seen that isomeric xylenes are not only possible, but that they exist ; and similar metamers of the tri- and tetramethyl derivatives are also known. On p. 283 was given a list of *mono*substituted benzenes, which, with the ~~alcoh~~ ~~of~~ ~~radicals~~ ~~higher~~ ~~than~~ ~~methyl~~ : the members of the two series which contain the same number of carbon atoms are obviously metameric. In addition to the members of the two series in question, we are acquainted with numerous cases of metamerism where *different radicals* replace hydrogen in benzene ; thus, not only have trimethylbenzenes, $C_6H_3(CH_3)_3$, been discovered, but we also know the metameric mono-substituted propylbenzene, $C_6H_5(C_3H_7)$, and the metameric ethyl-methylbenzene, $C_6H_4(C_2H_5)CH_3$—a disubstituted benzene containing different radicals ; but these derivatives are summed up in the expression, C_9H_{12}. No less than eight metameric bodies of this formula exist, and the number in the next group, $C_{10}H_{14}$, is much greater.

It would obviously confuse the student at this stage to enter into further details concerning these hydrocarbides and their very numerous derivatives ; we shall therefore only indicate the relations of a few well-known compounds to benzene and its higher homologues.

Phlorglucol and *Pyrogallol*, $C_6H_3(OH)_3$, are two metameric trihydroxybenzenes, or triphenols. These bear somewhat the same relation to benzene that glycerine does to propane. *Phlorglucol* is a sweet, crystalline body, obtained by the hydrolysis of *phloridzin*, a compound present in the roots of many fruit

trees ; it is also formed by heating catechu, kino, and certain other astringent principles with caustic potash. Phlorglucol is a *symmetrical* [1] trihydroxybenzene—that is to say, its hydroxyl groups replace hydrogen in benzene at the positions 1 : 3 : 5 (see p. 293).

Pyrogallol, or 'pyrogallic acid,' is an *unsymmetrical* triderivative, its hydroxyl replacing hydrogen at 1 : 2 : 4. It is produced when gallic acid, $C_6H_2(OH)_3COOH$, is heated ; carbon dioxide being evolved, while pyrogallol sublimes. It is a light crystalline body, easily soluble in water and alcohol ; it is a powerful reducing agent, and is extensively used for that purpose in photography ; it is most energetic in presence of alkalies, and, since such a solution rapidly absorbs free oxygen, it is employed in the analysis of air (see Experiments 83 and 89). With ferric chloride its solution gives a fine dark purple colour, and with calcium hydrate, violet.

Mesitylene and *pseudo-cumene* are two trimethyl-benzenes, $C_6H_3(CH_3)_3$. The first of these is the symmetrical compound 1 : 3 : 5, and is remarkable as a product of the dehydration of *acetone* by oil of vitriol ; it was discovered by Sir Robert Kane—

$$3(CO(CH_3)_2) = C_6H_3(CH_3)_3 + 3H_2O.$$
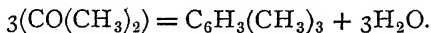
It is also met with in the fraction of coal-tar oils boiling between 160° and 170°, along with its metamer, *pseudo-cumene*, which is the unsymmetrical compound

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[1] In most trisubstituted benzenes we can recognise three metamers : the *symmetrical*, as above, 1 : 3 : 5 ; the *unsymmetrical*, as in pyrogallol, 1 : 2 : 4 ; and the *consecutive*, 1 : 2 : 3 positions.

1 : 3 : 4. Mesitylene affords the three following acids on careful oxidation :—

Mesitylenic acid .	.	$C_6H_3(CH_3)_2COOH$
Uvitic	„ .	.	$C_6H_3CH_3(COOH)_2$
Trimesic	„ .	.	$C_6H_3(COOH)_3$

Oil of cumin, or caraway, contains the hydrocarbide $C_6H_4(CH_3)C_3H_7$; it is a para, or 1 : 4 compound, and is named *paracymene.*[1]   *Thymol,* or 'thyme camphor,' is probably an unsymmetrical hydroxyparacymene,

$$C_6H_3(CH_3)C_3H_7(OH).$$
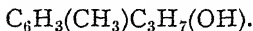
Mellitic acid, $C_6(COOH)_6$, corresponds to hexamethylbenzene, $C_6(CH_3)_6$, whose methyl groups have been oxidised to carboxyl. Its aluminium salt constitutes the mineral *mellite,* or honeystone (so named from its colour and appearance), met with in beds of lignite. It is also formed in small quantity when charcoal is oxidised by potassium permanganate in presence of free alkali. In nature it doubtless results from the limited action of air on the cellulose. Heated with lime, mellitic acid gives benzene, as do *all the carboxyl* derivatives of benzene when similarly treated.

$$C_6(COOH)_6 = C_6H_6 + 6CO_2.$$
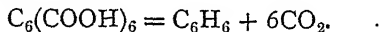
Another group of hydrocarbides and a few of their derivatives remain to be noticed before we pass from this branch of the subject. Hitherto we have

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[1] The same hydrocarbide is obtained by heating camphor with dehydrating agents,

seen that homologues of benzene are either mono-substituted, as those included in the list on p. 283, or polysubstituted, as are those given on p. 297. But it is obviously possible to regard toluene, or methyl-benzene, as a methane, or marsh-gas derivative, *i.e.* as phenylmethane. If this view be tenable, it is further evident that higher phenyl-substituted methanes should exist, for example :—

Phenylmethane (toluene) . . $(C_6H_5)CH_3$
Diphenylmethane . . . $(C_6H_5)_2CH_2$
Triphenylmethane . . . $(C_6H_5)_3CH$

The di- and trisubstituted methanes have been produced simultaneously by Friedel and Crafts, by means of their important aluminium chloride reaction ; they use chloroform to supply the CH group, and mix it with benzene. When aluminium chloride is added to the mixture, much hydrochloric acid gas is evolved ; at the end of the reaction the residue is washed and fractionated in vacuo, then diphenyl-methane first distils, and triphenylmethane after ; the latter is obtained in flat crystals which melt at 92° ; it results from the following reaction :—

$$3C_6H_5H + CHCl_3 = (C_6H_5)_3CH + 3HCl.$$
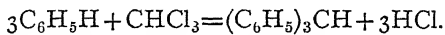
If carbon tetrachloride be substituted for chloroform, the compound $(C_6H_5)_3CCl$ is produced, and this, when treated with water, decomposes thus—

$$(C_6H_5)_3CCl + HOH = (C_6H_5)_3C - OH + HCl.$$
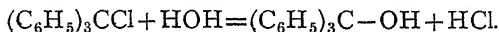
The product is the phenyl representative of trimethyl-carbinol (see p. 110).

Triphenylmethane, when acted upon by nitric acid, affords the nitroderivative *trinitrophenylmethane*, which, on reduction, yields *triamidophenylmethane*, or ' paraleucaniline,' thus—

$$(C_6H_4NO_2)_3CH \text{ becomes } (C_6H_4NH_2)_3CH.$$
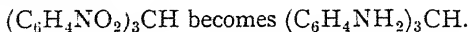
Leucaniline can afford an imide compound termed *pararosaniline*, and this is a lower homologue of the base *rosaniline* (see p. 271), whose salts and derivatives are met with in many of the magnificently coloured aniline dyes. These relations appear when the formulæ are compared as under :—

Triphenylmethane.	.	$C_{19}H_{16}$
Paraleucaniline	.	$C_{19}H_{13}(NH_2)_3$
Pararosaniline	.	$C_{19}H_{12}(NH_2)_2NH$
Rosaniline	.	$C_{20}H_{14}(NH_2)_2NH$

CHAPTER LXIV.

THE changes which can be effected in the 'side chains' of benzene derivatives have hitherto been referred to incidentally ; but we must now examine the simplest side-chain compound, toluene, in such a way as to give some definite knowledge of the conditions under which the benzene residue or the replacing radical can respectively be attacked. Before entering upon this it is well to point out the chief sources and characters of

Toluene,[1] or *methylbenzene*, C_7H_8 or $C_6H_5 - CH_3$. We have already learned that this hydrocarbide can

[1] So named because separated in the distillation of tolu balsam.

be obtained by replacing bromine in monobromo-benzene by Friedel and Crafts's and Fittig and Tollens's reactions, hence its constitution is certain (see p. 282); but it is separated in large quantity during the fractionation of the light coal-tar oils for benzene (see p. 258), it can therefore be easily purchased for experimental use.

Toluene is a mobile liquid of sp. gr. 0·872 at ordinary temperature; it does not solidify at 20°, hence it is readily distinguished from benzene, which solidifies at − 12°; its boiling point is 111°. It does not mix with water, but is easily miscible with strong alcohol, ether, and bisulphide of carbon. It burns with a very smoky flame.

It is evident that bromine should be capable of replacing hydrogen in either the benzene residue of toluene or in the methyl group, so as to form one or other of the following metameric compounds :—

$$C_6H_4Br(CH_3) \qquad \text{or} \qquad C_6H_5(CH_2Br).$$
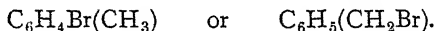
In the first case a disubstituted benzene would be obtained, one hydrogen atom being replaced by methyl, the other by bromine; hence, three metameric bromotoluenes should exist. But no metamer of the second compound should be obtained. We shall now examine the action of bromine on toluene.

Experiment 790.—Into a flask externally cooled by water pour about 12 c.cs. of toluene, then add less than half a gram of iodine, and gradually drop in 5 c.cs. of bromine. Hydrobromic acid is evolved; hence the experiment must be made under a good draught to get rid of the fumes. The reaction soon

slackens, and then slowly proceeds ; remove the flask from the cold water, and set it aside in a dark place for a day. The brown liquid product is then to be shaken up with much water and caustic soda gradually added, until the excess of bromine and iodine have been removed. The liquid when separated from water and distilled gives at first some unchanged toluene (at 111°), and then the boiling-point rises to 180°, and the rest passes over between that temperature and 185°. This liquid consists of C_7H_7Br.

By cold it is possible to separate this liquid into metameric compounds, one a crystalline body which melts at 28° and boils at 155° ; the other a liquid which does not solidify when cold, and boils at 151°. Both compounds exhibit as much indifference to chemical agents as monobromobenzene does. The crystals can afford *paraxylene* (1 : 4) by Fittig's method, and the liquid can give a derivative of *orthoxylene* (1 : 2). Consequently the former is parabromotoluene and the latter orthobromotoluene. A metameric metabromotoluene is also known, but does not appear to be formed during this action of bromine on toluene.

It is clear, then, that when the action takes place at a *low temperature*, bromine only replaces hydrogen in the benzene residue.[1]

Let the experiment be repeated with the difference that double volumes are used, and the toluene is heated *nearly to its boiling-point and freely exposed to sunlight*, at the same time that a current of carbon dioxide gas

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[1] Three corresponding chlorotoluenes are known.

carrying with it the vapour of bromine slowly bubbles through the hot liquid. This is easily managed by placing the 10 c.cs. of bromine in a small flask provided with a cork through which two glass tubes pass, one leading the carbon dioxide gas over the warmed bromine, the other conveying the gaseous mixture through the hot toluene. The bromine is rapidly used up in direct sunlight, and hydrobromic acid is evolved. When all the bromine has been vaporised, the liquid in the flask is distilled. At first unchanged toluene passes over, · nd then a liquid of sp. gr. 1·44, which boils at 202°, and is represented by the formula C_7H_7Br. It is termed *benzyl bromide*. As we know the three possible bromotoluenes, and they all boil below 186°, it follows that the above liquid is a distinct compound, and, if our theory be correct, it is the 'side-chain' derivative $C_6H_5(CH_2Br)$ referred to at p. 304. We shall test this conclusion later on.

Chlorine gas passed through toluene heated on the water-bath in sunlight acts in a similar way to bromine; by continued action at a higher temperature chlorine ultimately displaces all the hydrogen of the side chain, and *phenyl chloroform* is obtained. The following formulæ represent the series of derivatives :—

Benzyl chloride . . .	$C_6H_5(CH_2Cl)$
Benzylene chloride or benzal chloride . . .	$C_6H_5(CHCl_2)$
Phenylchloroform . .	$C_6H_5(CCl_3)$

Having learned that substitution in the benzene residue of toluene takes place at low temperatures and

in the side chain at high temperatures aided by sunlight, we shall briefly notice the former series of products, as they resemble the benzene derivatives already worked with.

Nitric acid attacks toluene in the same way as benzene, producing metameric nitrotoluenes analogous to nitrobenzenes, without affecting the methyl group. The chief products of direct action are the *ortho* and *para* modifications :[1] —

Orthonitrotoluene, $C_6H_4NO_2(CH_3)$, a liquid, b.p. 223°
Para   „   „   „   crystals m.p. 54° „ 236°
Meta „   „   „   „   „ 16° „ 231°

By reduction the nitrotoluenes afford corresponding amide compounds, termed *toluidines.*

Orthotoluidine—$C_6H_4NH_2(CH_3)$—   b.p. 198°
Para   „   „   crystals m.p. 43° „ 198°
Meta   „   „   liquid   „ 197°

Commercial ' aniline ' always contains a considerable proportion of ortho- and paratoluidine, and the presence of these bodies is essential to the production of rosaniline and some of the other dyes.

Toluene affords three metameric sulphonic acids, and the ortho- and para-compounds, when fused with potassium hydrate, give the corresponding mona-

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[1] In cases of direct action of halogens or acids on toluene, the *ortho* and *para* compounds are those chiefly produced. This is commonly true in the production of disubstituted benzenes.

tomic phenols, termed *cresols*, or incorrectly, 'cresylic acids.'

Orthocresol .   .   . crystals m.p. 31° b.p. 188°
Para „   .   .   .   „   „   36° „   198°
Meta „   .   .   . liquid   „   201°

Crude coal-tar oil which boils between 195° and 210° contains much paracresol and some of the ortho variety.

The cresols, like the other *phenols* which are related to benzene and its homologues, as alcohols to hydrocarbides, are distinguished by the readiness with which their hydroxyl hydrogen is replaced by metals ; by their general resistance of oxidation, and the readiness with which they afford substitution compounds *without loss of hydroxyl*, as in the formation of bromo- and nitrophenols and sulphonic acids. In these respects the phenols are in contrast with all other alcohols of the ethylic type. Nevertheless, we have now to learn that alcohols of the latter type are known which are derivable from benzene homologues and are metameric with phenols.

Such an alcohol can be produced from the side-chain bromide, $C_6H_5(CH_2Br)$, by the following simple method, which when applied to the monobromotoluenes does *not* afford a phenol.

Experiment 791.—Into a flask provided with a vertical condenser pour 17 grams of the bromide produced in the last experiment (or 13 grams of the corresponding chloride), along with 200 c.cs. of water, then add the calcium hydrate obtained by slaking five or six grams of good fresh lime, and boil

the mixture for several hours, or until on checking the ebullition all liquid *heavier* than water has disappeared, and has been wholly replaced by an oily liquid *lighter* than the solution in which it was formed. Separate the oily compound in the usual way from water and distil it from a few small lumps of calcium chloride. An agreeably smelling liquid distils at 207°, which does not solidify on cooling, and is of sp. gr. 1·063. It does not mix with water, but is readily miscible with ether, alcohol, and carbon disulphide. This liquid is *benzyl alcohol*, $C_6H_5(CH_2OH)$, and is obtained from the side-chain bromide or *benzyl bromide* even more readily than is ethyl alcohol from ethyl bromide. It was discovered by Professor Cannizzaro.

$$2C_6H_5(CH_2Br) + Ca(OH)_2$$
$$\underbrace{\hspace{4cm}}_{\text{Benzyl bromide.}}$$
$$= 2C_6H_5(CH_2OH) + CaBr_2$$
$$\underbrace{\hspace{4cm}}_{\text{Benzyl alcohol.}}$$
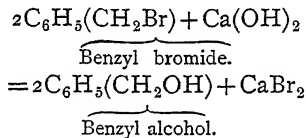
Esters are easily obtained by the action of acids, or acid chlorides, on this alcohol: thus with hydrochloric acid it gives benzyl chloride, with acetyl chloride, benzyl acetate, and so on; while benzyl ether, $(C_6H_5CH_2)_2O$, is produced by boiling the alcohol with dehydrating agents, such as zinc chloride or boracic anhydride.

Benzyl bromide or chloride acts on alcoholic ammonia very easily; on standing, crystals of *tribenzylamine*, $(C_6H_5CH_2)_3N$, separate after a few days. The solution contains the bromides of the ammoniums derived from dibenzylamine, $(C_6H_5CH_2)_2NH$, and

benzylamine, $(C_6H_5CH_2)NH_2$. The latter is meta-meric with the *toluidines*, but differs from them, not only in mode of generation, but in reactions. affording benzyl alcohol and nitrogen when treated with nitrous acid instead of a phenolic or an azocompound. Hence it is an analogue of ethylamine and its homologues ; moreover it can be formed by the action of nascent hydrogen on C_6H_5CN, or *benzonitrile*, just as ethyla mine can be produced by similar treatment by C_2H_5CN, or acetonitrile.

Analogy would lead us to expect that benzyl alcohol should afford an aldehyde and an acid on oxidation corresponding to ordinary aldehyde and acetic acid.

Experiment 792.—Pour a few drops of benzyl alcohol into a test-tube, add an equal volume of nitric acid, previously diluted with its own volume of water, and warm. Nitrous fumes are evolved, and the pleasant aromatic odour of *oil of bitter almonds* is developed. If the heat be continued, and a little more nitric acid be added from time to time, the oily liquid disappears, and the solution when cooled down affords crystals of *benzoic acid*. Now the oil of bitter almonds is the *aldehyde* of benzyl alcohol, and the acid is benzoic acid, obtained by further oxidation, thus :—

$$C_6H_5(CH_2OH)+O \quad = \quad C_6H_5(COH)+H_2O$$

Benzyl alcohol.   Oil of bitter almonds.

$$C_6H_5(COH)+O \quad = \quad C_6H_5(COOH)$$
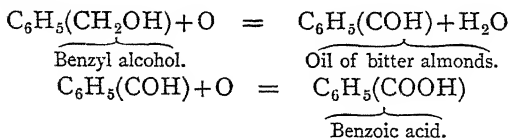
Benzoic acid.

In the production of benzoic acid or monocarboxyl benzene by this series of operations, we have the desired evidence that the substitution of bromine for hydrogen in toluene, effected at a high temperature and in sunlight, really took place in the methyl side chain, and not in the benzene residue. This conclusion is confirmed by the conversion of phenyl cyanide (benzonitrile) into benzoic acid. Both aldehyde and acid are obtained by many other methods, some of which we must now shortly notice.

Benzyl, or *benzoic aldehyde*, which is identical with the oil of bitter almonds, does not exist ready formed in the almonds, but results from the hydrolysis of a beautiful crystalline compound, termed *amygdaline*,[1] under the influence of a nitrogenised body termed *emulsine*, similar to diastase. The latter is present in much larger proportion in sweet almonds than in bitter : hence when the latter are bruised into a thin paste with water, the characteristic odour of the oil does not become perceptible until a similar paste of sweet almonds is added :—

$$C_{26}H_{27}NO_{11} + 2H_2O$$

$$\underbrace{\qquad\qquad}_{\text{Amygdaline.}}$$

$$= \quad \underbrace{C_6H_5(COH)}_{\text{Oil of bitter almonds.}} \quad + \quad \underbrace{CNH}_{\text{Prussic acid.}} \quad + \quad \underbrace{2C_6H_{12}O_6}_{\text{Glucose.}}$$
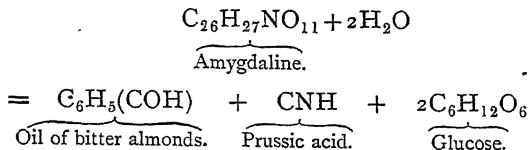
[1] The kernels of many other fruits as well as almonds contain this body ; for example, those of peaches and plums ; moreover, some leaves, such as the *laurel* (*cerasus*), appear to contain it, as they afford the oil and prussic acid when distilled with water ; hence the poisonous effects of laurel-water.

Amygdaline is therefore a *glucoside*, or a body capable of affording glucose on hydrolysis. The oil forms a feeble compound with the hydrocyanic acid produced at the same time ; hence the highly poisonous character of the ordinary bitter almond oil, for the latter is not dangerous when quite pure.

Artificial ' oil of bitter almonds ' is now prepared on a considerable scale from benzyl chloride (produced from boiling toluene) by a method discovered by Grimaux and Lauth, which consists in heating the chloride with a solution of lead or copper nitrate, when the following change occurs :—

$$2C_6H_5(CH_2Cl) + Pb(NO_3)_2 = 2C_6H_5(COH) + PbCl_2 + 2HNO_2.$$
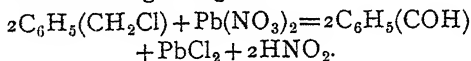
So obtained, the oil is a colourless liquid of characteristic almond odour ; its sp. gr. is 1·05, and it boils at 180°. It readily unites with acid sulphites ; with pentachloride of phosphorus gives *benzylidene chloride* $(C_6H_5CH)''Cl_2$; affords an oxime with hydroxylamine and combines with phenylhydrazine like the other CO compounds. With ammonia, however, three molecules of the aldehyde produce a compound termed *hydrobenzamide*, or *tribenzylidene diamine*—

$$\begin{array}{ll} C_6H_5CHO & (C_6H_5CH)''=N \\ C_6H_5CHO + 2NH_3 = & (C_6H_5CH)'' < \quad + 3H_2O \\ C_6H_5CHO & (C_6H_5CH)''=N \end{array}$$
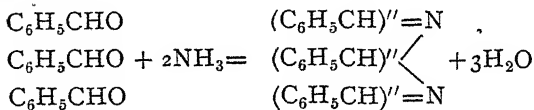
When the aldehyde is acted upon by nascent hydrogen, it is reduced to benzyl alcohol ; if exposed to the air, it takes up an atom of oxygen and affords benzoic acid. Heated with alcoholic solution of

caustic potash, Cannizzaro showed that the aldehyde undergoes the following interesting decomposition :—

$$2C_6H_5COH + HOK = C_6H_5(CH_2OH)$$

Benzyl aldehyde.   Benzyl alcohol.

$$+ C_6H_5(COOK)$$

Potassium benzoate.
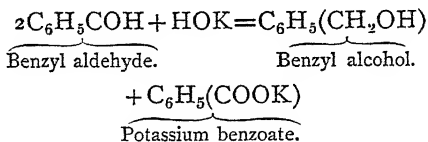
In this way both alcohol and acid can be easily obtained from bitter almond oil.

Benzoic acid, C_6H_5COOH, is, as we have seen, obtainable by oxidation of bitter almond oil, or by boiling it with caustic potash. When the potassium salt is purified by recrystallisation, it is dissolved in boiling water, and an excess of hydrochloric acid added, which sets free benzoic acid ; the latter then separates out on cooling the liquid. When heated to 140° the acid sublimes, and affords beautiful white feathery crystals, which usually have a somewhat aromatic odour. The acid is, however, most commonly obtained by carefully heating *gum benzoin* or *benjamin*, a resinous body, from which benzoic acid sublimes, and is collected. The acid dissolves in twelve parts of boiling water, though slightly in cold ; it easily dissolves in alcohol. It readily dissolves in alkalies, forming benzoates, while ferric chloride added to a solution of a neutral benzoate causes *a buff-coloured precipitate* of ferric benzoate.

Benzoic acid does not occur in the free state in the animal economy, but a derivative of it, named *Hippuric acid*, is met with in the urine of the horse and most of the herbivora. Hippuric acid, when boiled

for some time with hydrochloric acid, breaks up into benzoic acid and *glycosine* or amidacetic acid :—

$$C_9H_9NO_3 + H_2O = C_6H_5COOH + CH_2(NH_2)COOH$$

Hippuric acid.   Benzoic acid.   Glycosine.
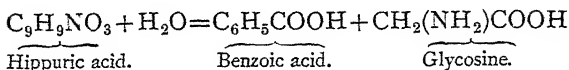
The synthesis of hippuric acid has been effected most simply by heating benzoic acid or benzoyl chloride (see below) with glycosine. A similar synthesis is performed in man: when benzoic acid is taken internally, hippuric acid appears in the urine. Hippuric acid is $CH_2(NHC_6H_5CO)COOH$, or *benzoyl glycosine.*

Benzoyl chloride, C_6H_5COCl, analogous to acetyl chloride, is obtained by the action of phosphorus pentachloride on benzoic acid. When the chloride acts upon a benzoate, *benzoic anhydride* $(C_6H_5CO)_2O$ is produced. When the chloride acts on ammonia benzamide is formed :—

$$C_6H_5COCl + NH_3 = C_6H_5CO—NH_2 + HCl.$$
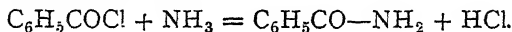
Ammonium benzoate, when heated, also affords *benzamide,* just as ammonium acetate gives acetamide.

When calcium or barium benzoate is very carefully heated, *benzophenone* or phenyl ketone is formed.

$$Ca(C_6H_5COO)_2 = CaCO_3 + CO{\Large\langle}{{C_6H_5}\atop{C_6H_5}} .$$
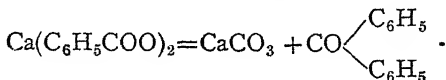
At the same time much *benzene* is produced. When benzoic acid is heated with an excess of calcium hydrate, only benzene is obtained, and in a very pure state :—

$$Ca(C_6H_5COO)_2 + Ca(OH)_2 = C_6H_6 + 2CaCO_3.$$
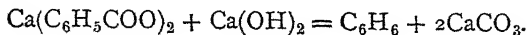
Acetophenone, or phenyl-methyl ketone, can be formed by heating a mixture of calcium acetate and benzoate ; the product $C_6H_5CO—CH_5$ is crystalline and melts at 20°, while it boils at 202°. A diketone termed *benzil*, $C_6H_5—CO—CO—C_6H_5$, is formed by heating with nitric acid the ketonic alcohol, $C_6H_5—CO—CH(C_6H_5)OH$, termed *benzoin*, which results from a remarkable condensation of two molecules of the aldehyde that takes place in presence of a little potassium cyanide boiled with it in alcoholic solution.

If benzyl bromide be boiled with potassium cyanide, we obtain benzyl cyanide $C_6H_5(CH_2—CN)$ by double decomposition, and this, when heated with potash, changes its cyanogen for carboxyl, affording the potassium salt of a new acid distinguished as *alpha-toluic acid*, in which carboxyl replaces the hydrogen of the *methyl*—

$$C_6H_5(CH_2—CN) + HOK + H_2O$$
$$= C_6H_5(CH_2—COOK) + NH_3.$$
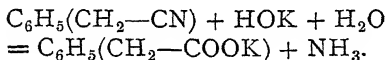
If we regard benzoic acid as phenyl-formic acid, *a*-toluic acid is phenyl-acetic acid—

Formic acid	. .	$H—COOH$
Benzoic acid	. .	$C_6H_5—COOH$
a-Toluic acid	. .	$C_6H_5—CH_2—COOH$

Three metameric toluic acids are known in which carboxyl replaces hydrogen of the *benzene residue*, leaving the methyl untouched ; these may be regarded as intermediate between the xylenes and phthalic acids, and are in fact obtained by partial oxidation

of the former. Their relations appear from the following :—

$$C_6H_4(CH_3)_2, \quad C_6H_4(CH_3)COOH, \quad C_6H_4(COOH)_2$$

<u>Xylenes.</u>   <u>Toluic acids.</u>   <u>Phthalic acids.</u>
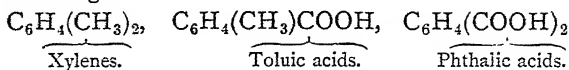
It is evident that in most of the benzylic compounds hitherto considered in this chapter, the benzene residues are wholly untouched, but it is clearly possible that in other cases, besides the toluic acids, the phenylic group should undergo change along with the methyl group. In fact, when benzoic acid is treated with very concentrated nitric acid, metameric nitrobenzoic acids are formed, and these can be reduced to amidobenzoic acids ;[1] similarly bromine and chlorine can afford bromo- and chloro-benzoic acids, sulphuric acid, sulphobenzoic acids, &c. It is evident, then, that we can recognise the three distinct classes of toluene derivatives represented by the following compounds :—

$$\overset{(1)}{C_6H_4(NO_2)CH_3} \quad \overset{(2)}{C_6H_3(COOH)} \quad \overset{(3)}{C_6H_4(NO_2)COOH}$$

<u>Nitrotoluene.</u>   <u>Benzoic acid.</u>   <u>Nitrobenzoic acid.</u>
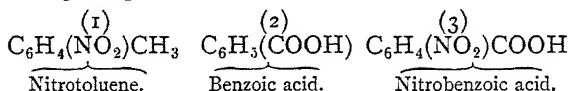
A very few of the most important representatives of class (3) must now be mentioned.

When the bromo-, chloro- or sulpho-benzoic acids are heated with caustic potash, the halogen or other group is replaced by hydroxyl and hydroxybenzoic acid, or a salt of it is formed :—

$$C_6H_4Br(COOH) + KOH = C_6H_4(OH)COOH + KBr.$$

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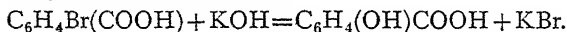
[1] Orthonitrobenzoic acid reduced by tin and hydrochloric acid gives the amido-acid $C_6H_4(NH_2)COOH$ (1 : 2), named *Anthranilic acid.*

The para- and meta-compounds are of no practical importance at present and need not be considered, but the ortho acid is the very valuable antiseptic *salicylic acid*, and can be obtained by the above method from any of the ortho-benzoic compounds. But a synthetic process of great interest was devised by the late Professor Kolbe of Leipzig, by which large quantities of salicylic acid are now prepared.

Experiment 793.—Dissolve 13 grams of good caustic soda in 30 c.cs. of water contained in a small retort, now add 30 grams of crystallisable phenol or carbolic acid and heat, sodium [1] phenylate is formed, and the liquid is carefully boiled down to dryness in the retort; when all the water has been driven off and the whole has cooled down somewhat, arrange the bulb on the water-bath and pass a stream of carbon dioxide through the retort for half an hour at 100° ; now heat still in the current of gas by means of an Argand lamp until phenol distils (183)°, then keep the temperature to this point until no more phenol comes over, and let the residue cool. The process must be conducted slowly throughout. The change that occurs is the following :—

$$2(C_6H_5ONa) + CO_2$$
$$= C_6H_4(ONa)COONa + C_6H_5OH,$$
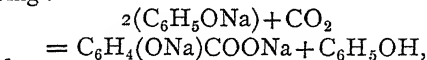
so that only half the phenol is converted. Dissolve the residue in as little water as possible, filter and add excess of hydrochloric acid which separates impure

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[1] If potash be used instead of soda, para-oxybenzoic acid is the chief product of the subsequent treatment, not salicylic acid.

salicylic acid. This can be purified by solution of the slightly washed crystals in alcohol containing a little ether, and subsequent evaporation. The pure acid can now be readily purchased.

This mode of generation of salicylic acid is good evidence of its structure ; it is obviously half phenol and half acid, like lactic acid. Moreover, it is an ortho-compound, because derivatives of it afford phthalic acid (q. v.) on oxidation.

Salicylic acid, $C_6H_4(OH)COOH$, when pure, is a white crystalline substance which melts at 156°, and can be distilled in a current of steam. It is slightly soluble in cold water, but easily and freely in boiling water, in alcohol and ether. When in solution it destroys the activity of bacteria and stops fermentation, therefore it is used extensively as an antiseptic. Ferric chloride gives a fine *violet colour* with its solution. Salicylic acid derives its name from *salicine,* a bitter crystalline glucoside derived from the willow and poplar. This undergoes hydrolysis like amygdaline, and breaks up into glucose and *saligenine,* a compound half alcohol and half phenol—

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + C_6H_4(OH)CH_2OH$$

Salicine.   Saligenine.   .
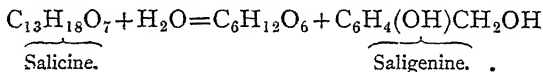
When saligenine is oxidised it gives first an aldehyde, which is identical with the *oil of meadow sweet (Spiræa Ulmaria)*, and then salicylic acid. An aldehyde identical with oil of meadow sweet is produced by an interesting reaction due to Reimar and Tiemann, which consists in heating sodium phenolate and excess of

caustic soda with chloroform, when the following re-
action takes place :—

$$C_6H_5ONa + CHCl_3 + 3NaOH$$
$$= C_6H_4(ONa)COH + 3NaCl + 2H_2O.$$
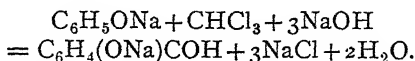
The addition of an acid sets free the oil which is
half aldehyde, half phenol, $C_6H_4(OH)COH$. On
oxidation this gives salicylic acid.

Oil of Wintergreen, or *Gaultheria procumbens*, con-
sists chiefly of methyl salicylate. This is readily
saponified and the free acid obtained. Salicylic acid
is easily acted on by the halogens, and mono- and
di- iodo-salicylic acids can be obtained by the direct
action of iodine. When the two former are carefully
treated with caustic potash, iodine is replaced by
hydroxyl. Thus, while salicylic acid itself can be ob-
tained by a similar method from benzoic acid, we
have the following series of hydroxyl derivatives of the
latter :—

Benzoic acid . . . C_6H_5COOH
Hydroxybenzoic acid . $C_6H_4(OH)COOH$
  = Salicylic acid
Dihydroxybenzoic acid . $C_6H_3(OH)_2COOH$
  = Protocatechuic acid
Trihydroxybenzoic acid . $C_6H_2(OH)_3COOH$
  = Gallic acid.
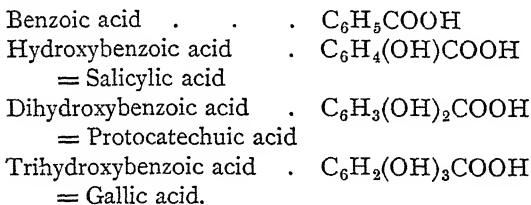
Protocatechuic acid, from which *pyrocatechine* can
be prepared, is a 1 : 2 : 4 compound. It is also ob-
tained by fusing catechu or kino with four times its
weight of caustic potash and dissolving the p   t
in water. The acid is set free by diluted sulphuric

acid, and the mixture is shaken up with ether in which protocatechuic acid dissolves, and from which it can be obtained in crystals that give a green colour with ferric chloride changed to red by caustic alkalies, like pyrocatechine. The latter and carbon dioxide are produced when the crystals are carefully heated:—

$$C_6H_3(OH)_2COOH = C_6H_4(OH)_2 + CO_2.$$
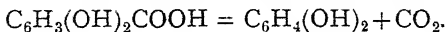
$C_6H_3(OH)(OCH_3)COOH$, methyl protocatechuic acid, is identical with *vanillic acid*, formed by oxidation of *vanillin*, $C_6H_3(OH)(OCH_3)COH$, which is a crystalline aldehyde of strong aromatic odour extracted by ether from the pods of orchidaceous plants. Dimethylprotocatechuic acid appears to be identical with *veratric acid*, $C_6H_3(OCH_3)_2COOH$, derived from certain of the *hellebores*.

Gallic acid, or trihydroxybenzoic acid, is chiefly obtained by hydration of *tannin*, $C_{14}H_{10}O_9$. The latter is a common constituent of astringent vegetable extracts, but is principally prepared from gall-nuts and oak bark by the following process :—Powdered gall-nuts are exposed for two or three days to moist air, and then made into a thin paste with ether containing a twentieth of its volume of water. After standing some hours the paste is expressed and the clear liquid is distilled ; the ether is thus recovered, while a strong aqueous solution of tannin is left ; this is evaporated to dryness in thin layers, and the tannin obtained in yellow glistening scales or powder. Tannin[1] is very slightly soluble in anhydrous ether, but

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[1] Several modifications of tannin are supposed to exist.

is easily soluble in alcohol and in water. It acts as if it were a monobasic acid.

Experiment 794.—Dissolve some tannin in water, and divide the solution in two parts. (*a*) Add to this ferric chloride; a bluish-black or 'inky' colour is at once produced. Common writing ink is produced by adding an iron salt to aqueous extract of gall-nuts or other materials containing tannin, and slightly 'thickening' the dark liquid by addition of gum arabic and sugar. (*b*) Add a few drops of *gelatine* solution; a yellowish-white precipitate is immediately formed, which contains tannin and gelatine, and does not decompose. The process of 'tanning,' or converting skins into *leather*, depends on the production of this substance. Skins, after thorough cleansing from hair, &c., are soaked for a long time in solutions of oak bark or other cheap materials containing tannin. The latter slowly unites with the gelatine-like constituents of the skin, which are thus completely protected from the decomposition they would otherwise undergo.[1]

Tannin was long regarded as a glucoside, but it does not afford sugar on hydrolysis; on the contrary, when its solution is heated with diluted sulphuric acid for some time, it is wholly converted into gallic acid, whose constitution is determined by its formation from diiodosalicylic acid. The hydration may be represented thus :—

$$C_{14}H_{10}O_9 + H_2O = 2C_6H_2(OH)_3COOH$$
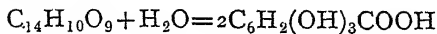
[1] Tannin added to tartar emetic solution forms an insoluble tannate of antimony; hence liquids rich in tannin are used as antidotes for antimony.

According to this, tannin is possibly a hemi-anhydride or a digallic acid, but its structure is not yet definitely known.

In practice the conversion of tannic into gallic acid is determined by boiling the gall-nuts with diluted sulphuric acid for half an hour ; the liquid is filtered while hot, and on cooling deposits gallic acid in small crystals.   These are purified by recrystallisation from boiling water, animal charcoal being used to remove colouring matter.

Gallic acid, as commonly met with, is a light highly crystalline powder, of a pale yellowish colour, and contains one molecule of water of crystallisation. It dissolves in three parts of boiling water, but requires one hundred of cold water for solution.   It dissolves easily in alcohol.

Experiment 795.—Dissolve a little gallic acid in boiling water and divide in two parts.

(a) Add ferric chloride ; a bluish-black colour is produced, like that caused by tannin.

(b) Add gelatine, and note that no precipitate is formed.

Thus gallic acid is readily distinguished from tannin by its slight solubility in cold water and its failure to precipitate gelatine.

When carefully heated, gallic acid is resolved into pyrogallol (see p. 298) and carbon dioxide—

$$C_6H_2(OH)_3COOH = C_6H_3(OH)_3 + CO_2.$$
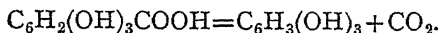
Before closing this chapter, and with it an outline of the derivatives of the C_nH_{2n-6}, or benzene series, it is desirable to point out the genetic relations with

them of a few of the hydrocarbides of other series, which will be referred to later on.

It has been already mentioned that monobromo-benzene or phenyl bromide treated with sodium gives *diphenyl*, $C_{12}H_{10}$; similarly benzyl bromide affords *dibenzyl*, $C_{14}H_{14}$. When the latter hydrocarbide is passed over strongly heated lead oxide, it loses two atoms of hydrogen, and *stilbene*, $C_{14}H_{12}$, is formed ; this readily combines with two atoms of bromine, and affords a dibromide, which, when heated with alcoholic potash, loses two molecules of HBr, and leaves the hydrocarbide *tolane*, $C_{14}H_{10}$. Thus dibenzyl by loss of hydrogen affords the following compounds :—

$$\text{Dibenzyl} \qquad \begin{array}{c} C_6H_5\text{—}CH_2 \\ | \\ C_6H_5\text{—}CH_2 \end{array}$$

$$\text{Stilbene} \qquad \begin{array}{c} C_6H_5\text{—}CH \\ \| \\ C_6H_5\text{—}CH \end{array}$$

$$\text{Tolane} \qquad \begin{array}{c} C_6H_5\text{—}C \\ \||| \\ C_6H_5\text{—}C \end{array}$$
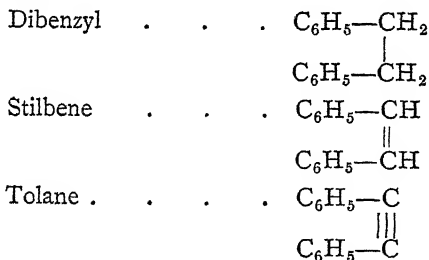
The last compound is sometimes termed 'acetenyl benzene,' but that term is more correctly reserved for the hydrocarbide we shall refer to at page 336 of the next chapter. Tolane is metameric with *anthracene*.

CHAPTER LXV.

STYRENE OR CINNAMENE—CINNAMIC ACID—ITS ALDE-
HYDE. CINNAMYL ALCOHOL. CINNAMIC ACID FROM
TOLUENE — BAEYER'S SYNTHESIS OF INDIGO —
NATURAL INDIGO—INDICAN—DYER'S SOLUTIONS—
WHITE INDIGO—ISATINE—DIOXINDOLE, OXINDOLE,
INDOLE — PHENYL-ACETYLENE — NAPHTHALENE—
BAEYER AND PERKIN'S SYNTHESIS OF NAPHTHALENE
—METAMERIC MONOSUBSTITUTED NAPHTHALENES
—NAPHTHOLS—NAPHTHAQUINONES.

BERTHELOT found that the liquid he obtained on
strongly heating acetylene, as in Experiment 772,
contained other hydrocarbides in addition to benzene.
Amongst these was one whose formula proved to
be C_8H_8, and which obviously resulted from the
condensation of four molecules of acetylene—

$$4(C_2H_2) = C_8H_8.$$
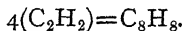
A hydrocarbide of the same composition is obtained
when liquid *storax* is distilled with water, and is
named *styrene.* We shall now examine the material
from which the hydrocarbide is obtained.

Liquid storax is the exudation from a shrub,
Styrax officinalis (liquid amber), which grows freely in
Greece and the Levant. When genuine [1] it is a viscid

[1] It is very frequently adulterated.

dark yellow liquid, about the consistence of honey, but becomes more fluid when heated : it has an agreeable aromatic odour. It is used in medicine as *Styrax præparatus*, B.P.

Experiment 796.—Introduce about 30 grams into a retort along with 15 grams of crystallised sodium carbonate and 300 c.cs. of water. Boil rapidly and distil over about half the water. The distillate is mixed with some oily drops of *styrene*, which can be separated. The residual liquid in the retort is poured off the resinous residue [1] and filtered. Enough diluted sulphuric acid is added to cause a slight precipitate ; it is again filtered and excess of acid mixed with the filtrate. A yellowish-white precipitate is obtained of *cinnamic acid*, $C_9H_8O_2$.[2]

We shall now enter into some details about these products.

Styrene, C_8H_8, styrole, or cinnamene, is a pleasant-smelling, mobile liquid, of sp. gr. 0·925°, which boils at 144°.

Styrene contains two atoms less of hydrogen than the corresponding metameric benzene homologues, *xylene*, C_8H_{10}, and *ethyl-benzene*, C_8H_{10} ; styrene is therefore a member of another series of hydro-carbides, C_nH_{2n-8}. Its mode of generation from acetylene indicates that it probably contains a benzene residue. In confirmation of this Berthelot showed

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[1] This contains a liquid substance termed *styracine*, which will be again referred to. The residue should be preserved.

[2] This acid can also be extracted by boiling balsam of Peru with sodium carbonate and treating the solution as above.

that it is formed when a mixture of benzene vapour and ethylene gas is passed through a red-hot tube. As this mode of generation could be explained by the equation—

$$C_6H_6 + C_2H_4 = C_6H_5C_2H_3 + H_2,$$
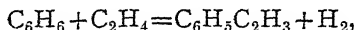
the inference is obvious that styrene is a side-chain derivative of benzene, and should consequently be obtained by removing two atoms of hydrogen from ethyl-benzene. The validity of this reasoning is established, since it is found that ethyl-benzene, when converted into bromethyl-benzene and heated with alkali, loses HBr and affords styrene—

$$\underbrace{C_6H_5(CH_2—CH_3)}_{\text{Ethyl-benzene.}} \quad : \quad \underbrace{C_6H_5(CH_2—CH_2Br)}_{\text{Bromethyl-benzene.}}$$

$$\underbrace{C_6H_5(CH=CH_2)}_{\text{Styrene.}}$$
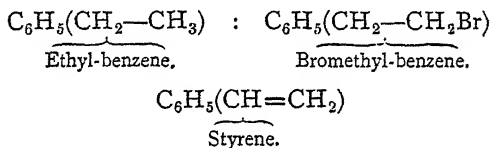
It is therefore evident that styrene may be regarded as ethylene with one hydrogen atom replaced by phenyl, and the readiness with which it unites with two atoms of bromine or chlorine to form addition compounds accords with that view, while proving that styrene is an *unsaturated* hydrocarbide.

We have already seen that styrene is associated in nature with cinnamic acid, and it is found that the latter, when distilled with lime, gives styrene (often termed *cinnamene* in consequence)—

$$\underbrace{C_9H_8O_2}_{\text{Cinnamic acid.}} \quad = \quad \underbrace{C_8H_8}_{\text{Styrene.}} + CO_2$$
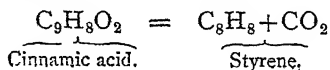
This is exactly analogous to the decomposition of benzoic acid when heated with lime—

$$C_7H_6O_2 \quad = \quad C_6H_6 + CO_2$$

<u>Benzoic acid.</u>   <u>Benzene.</u>
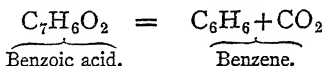
Hence styrene is related to cinnamic acid as benzene to benzoic acid; that is—

$$C_6H_5(CH=CH_2) \; : \; C_6H_5(CH=CH—COOH)$$

<u>Styrene.</u>   <u>Cinnamic acid.</u>
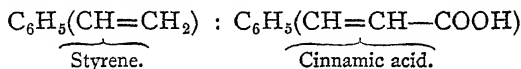
In which case cinnamic acid is *phenyl-acrylic acid*; and we infer that its aldehyde is *phenyl-acrolein*, derivable from *phenyl-allyl alcohol*, which is the side-chain hydroxyl derivative of *phenyl-allyl*, or allyl-benzene. These relations appear from the following :—

Acrylic acid . .	$H—CH=CH—COOH$
Phenyl-acrylic (cinnamic) acid . .	$C_6H_5—CH=CH—COOH$
Phenyl-acrolein . .	$C_6H_5—CH=CH—COH$
Phenyl-allyl alcohol .	$C_6H_5—CH=CH—CH_2OH$
Phenyl-allyl (allyl-benzene)[1] . . .	$C_6H_5—CH=CH—CH_3$

The hydrocarbide is therefore related to the alcohol and cinnamic acid as toluene (methyl-benzene) is to benzyl alcohol and benzoic acid (see p. 310).

The aldehyde *cinnamic aldehyde*, or phenyl acrolein, is the chief constituent of the essential oils of *cinnamon* and *cassia*, which generally contain some cinnamic acid as well. The aldehyde and acid alike

[1] This is $C_6H_5(C_3H_5)$, the next higher homologue of styrene, which is *vinyl-benzene* –$C_6H_5(C_2H_3)$, or *phenyl ethylene*.

derive their special names from their chief source 'cinnamon,' the thin inner bark of *Cinnamomum zeylanicum.*

Experiment 797.—Shake up in a narrow stoppered bottle or tube about 10 c.cs. of essential oil of cinnamon with its own volume of colourless but strong nitric acid, and let the mixture stand in a cool place for a few hours. Fine crystals separate, which consist of a feeble and unstable compound of the aldehyde with nitric acid. Drain away the liquid and mix the crystals with water; the feeble compound is broken up and the aldehyde separates as an oil of sp. gr. 1·03, which is more or less decomposed by distillation alone, though readily distilled with aqueous vapour. It has the characteristic cinnamon odour. It exhibits the usual aldehydic characters, combining with acid sulphites [1] and with ammonia; in the latter case, like other aromatic aldehydes, it forms *hydrocinnamide*, just as bitter almond oil affords hydrobenzamide (see p. 312).

The alcohol, *cinnamyl alcohol*, C_9H_9OH, or 'styrone,' is most easily obtained from the resinous residue left in Experiment 796. This contains an oily liquid named *styracine*, which is *cinnyl cinnamate*, C_6H_5—CH=CH—COO—C_9H_9; when the whole material is distilled with strong caustic soda, the ester is saponified, and the distillate contains the alcohol, which is separated as a crystalline solid on the addition of common salt, in whose solution it is much less

[1] When the crude oil is shaken up with acid sulphite of potassium, the aldehyde compound separates; from the latter the pure aldehyde can be obtained by careful addition of dilute sulphuric acid.

soluble than in pure water. This is separated and crystallised from a little water; the alcohol is then obtained in soft silky crystals, having an odour of hyacinths. They melt at 33°, and when carefully oxidised afford the aldehyde and then cinnamic acid, which is also quickly obtained when the aldehyde is exposed to air along with water.

Experiment 798.—Boil the crude cinnamic acid obtained in Experiment 796 with sufficient water to nearly dissolve it, then filter quickly and cool, when the nearly pure acid crystallises out in small needles, as it is very slightly soluble in cold water. *Pure cinnamic acid* melts at 133° and boils at 303°; but it can be distilled along with water vapour. It is easily soluble in alcohol and benzene.

Experiment 799.—Dissolve a little of the acid in water with the aid of ammonia, boil off the excess of the latter so as to get a neutral ammonium cinnamate, and add *ferric chloride* to the solution; a buff-coloured precipitate is obtained very like that caused by a benzoate; but the two acids can be distinguished by *manganese chloride*, which gives a whitish precipitate with a cinnamate, but does not precipitate a benzoate. Moreover, a cinnamate mixed with chromic acid solution becomes yellow and gives the odour of cinnamon and *bitter almond oil*, but the acid itself and its salts are inodorous when pure.

A knowledge of the fact that cinnamic acid easily affords benzyl aldehyde on decomposition led to the use of the latter in attempts to effect the synthesis of the acid, which Mr. W. H. Perkin successfully accomplished by heating benzyl aldehyde with acetic anhydride and sodium acetate. This, which is known

as 'Perkin's reaction,' has been considerably simplified by Dr. Caro, of Ludwigschäfen, and is now the starting-point in the manufacture of cinnamic acid in quantity for the production of *artificial indigo*.

Caro commences with toluene $C_6H_5(CH_3)$, which he converts into *benzylene dichloride*, $C_6H_3(CHCl_2)$, by the continued action of chlorine on boiling toluene, and heats the product directly with sodium acetate, when the following change occurs :—

$$C_6H_5(CHCl_2) + CH_3—CO—ONa$$
$$= C_6H_5(CH=CH—COOH) + NaCl + HCl.$$
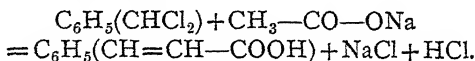
The conversion of the cinnamic acid so obtained into indigo is effected by the following series of operations, which are now carried out on a large scale.

1. *Orthonitro-cinnamic acid is prepared.*—The nitration of the acid itself is a matter of great difficulty, as it easily breaks up, but *ethyl cinnamate* is nitrated with facility ; consequently the latter is formed by heating cinnamic acid with alcohol, and the ester is mixed with well-cooled nitric acid. A solid mixture of ortho- and para-nitrocinnamate of ethyl is obtained, from which the former is separated by solution in alcohol. The para-compound is not dissolved, and is not further required. The ortho-ester is then saponified and the free acid obtained—

$$C_6H_5(CH=CH—COOH)$$

Cinnamic acid.

$$: \quad C_6H_4(NO_2)CH=CH—COOH$$

Orthonitro-cinnamic acid.
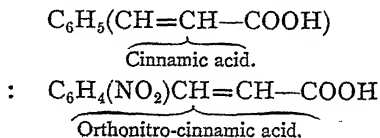
2. *Orthonitro-phenylpropiolic acid is formed.*—In order to effect this conversion it is necessary to remove two atoms of hydrogen from the nitro-acid, and this is effected in two stages. Cinnamic acid, like all acrylic acids, can unite directly with two atoms of bromine, and the nitro-acid retains this power, so that by mere addition the dibromide is readily formed :—

$$C_6H_4(NO_2)CH = CH—COOH$$

$$\underbrace{}_{\text{Ortho-acid.}}$$

$$C_6H_4(NO_2)—CHBr—CHBr—COOH$$
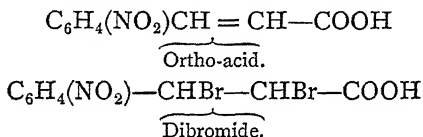
$$\underbrace{}_{\text{Dibromide.}}$$

When the dibromide is treated with the exact quantity of caustic soda necessary, two molecules of HBr are eliminated, and the sodium salt of the propiolic acid [1] is formed. From this solution hydrochloric acid precipitates the propiolic acid, which is simply drained, pressed, and sent to the dyers as 'propiolic paste.' Its formation from the dibromide is thus represented :—

$$C_6H_4(NO_2)CHBr—CHBr—COOH$$

$$\underbrace{}_{\text{Dibromide.}}$$

$$C_6H_4(NO_2)—C{\equiv}C—COOH$$

$$\underbrace{\phantom{C_6H_4(NO_2)—C{\equiv}C—COOH}}_{\text{Orthonitro-phenylpropiolic acid.}}$$
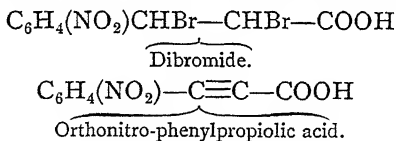
3. *Conversion of the propiolic acid into indigo.*—This consists in dissolving the acid in a dilute alkaline solution and adding grape sugar, potassium xanthate, or similar feeble reducing agent ; *indigo blue* separates

---

[1] That is, an acid of the acetylene series whose members contain two atoms of hydrogen less than the corresponding member of the acrylic acid series (see p. 237).

out on standing or warming, and is found to be identical in composition and properties with that obtained from the plant. This change probably takes place in two stages. (*a*) The propiolic acid loses CO_2 under the influence of the alkali and yields *isatine*, thus :—

$$C_6H_4(NO_2)\!-\!C\!\equiv\!C\!-\!COOH$$

$$\underbrace{}_{\text{Propiolic acid.}}$$

$$=C_6H_4\!\!\underset{\displaystyle CO}{\overset{\displaystyle NH}{\Big\langle}}\!\!\Big\rangle CO+CO_2$$
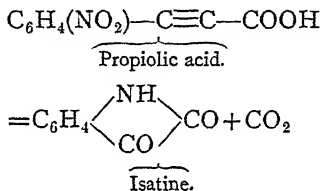
$$\underbrace{}_{\text{Isatine.}}$$

(*b*) Isatine then parts with an atom of oxygen to the reducing agent, and indigo blue [1] is formed—

$$C_6H_4\!\!\underset{\displaystyle CO}{\overset{\displaystyle NH}{\Big\langle}}\!\!\Big\rangle C$$
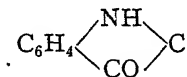
This formula must probably be doubled, but its relation to isatine is more evident when written as above.

The use of propiolic acid instead of natural indigo is not yet considerable, chiefly owing to the high price of the former. This difficulty would be overcome if a cheap substitute for bromine were to be found.

We owe the beautiful synthesis just explained to Professor Baeyer, of Munich, to whom we are indebted for other methods of building up indigo blue that we cannot stop to trace.

[1] Propiolic acid is decomposed and indigo blue produced from it *in the tissue* during the process of dyeing. A purer colour is obtained in this way than with natural indigo.

Indigo blue is naturally obtained from the plants *Indigofera tinctoria* and *Isatis tinctoria*, or 'woad,' by very simple treatment. The leaves and stalks are thrown into wooden vats with some water and allowed to ferment. During this process a glucoside termed *indican* dissolves and undergoes hydrolysis into indigo blue, and a peculiar form of sugar termed *indiglucin*, thus, according to Schunck of Manchester :—

$$C_{26}H_{31}NO_{17} + 2H_2O = C_8H_5NO + 3C_6H_{10}O_6$$

| Indican. | | Indigo. | Indiglucin. |
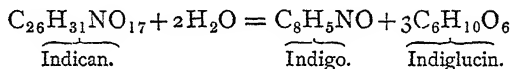
When sufficiently fermented the liquid is drawn off into shallow vats, where it is freely exposed to the air; here blue indigo separates as an insoluble precipitate, which is collected, pressed, and dried for market. In this condition it occurs in cakes which, when broken, have a fine coppery reflection. If cautiously heated it can be sublimed in small· but fine crystals. When strongly heated it affords *aniline*, which was first obtained in this way. Indigo is dissolved for dyeing purposes by either of the two following methods.

Experiment 800.—Heat in a flask one gram of indigo in fine powder with 20 c.cs. of the strongest sulphuric acid (better if fuming), and heat on the water-bath for an hour. When cold, dilute with 50 c.cs. of sulphuric acid ;[1] a blue liquid is obtained, which will bear dilution with much water without precipitation, as the soluble sulphuric compound is formed, $C_{16}H_9(SO_2OH)N_2O_2$, sometimes termed 'sulphin-

[1] This solution serves for testing for nitric acid (q.v.), chlorates, &c.

digotic acid.' The existence of this body points to the double formula as the correct one for indigo blue.

Experiment 801.—Rub into a thin cream with water about one gram of indigo and five grams of slaked lime, pour into a flask, and dilute with 300 or 350 c.cs. of boiling water containing four grams of ferrous sulphate in solution, cork the flask well, shake up, and then allow to stand. When the precipitate subsides, a yellowish supernatant liquid is left. This represents the dyer's 'cold vat.' Take a small piece of white calico, having first cleansed thoroughly in boiling water, soak it in the clear liquid in the flask, and then remove into the air. It soon acquires a *blue* colour.[1] The explanation of these changes is this. Ferrous hydrate reduces blue indigo to white indigo, which dissolves. Thus :—

$$C_6H_4 < \begin{matrix} NH \\ CO \end{matrix} > C \qquad : \qquad C_6H_4 < \begin{matrix} NH \\ C(OH) \end{matrix} > C$$

Blue indigo.   White indigo.
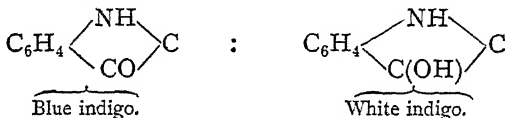
When the white indigo solution in the fibre is exposed to the air, it loses the atom of hydrogen again. Indigo, when carefully oxidised with nitric acid, affords *isatine*, $C_8H_5NO_2$.

Experiment 802.—Boil 25 grams of finely powdered indigo with 100 c.cs. of water in a large dish and gradually add 12 to 15 c.cs. of strong nitric acid. When the *blue* colour has been changed, and all strong

[1] Some of the yellowish liquid mixed with a few drops of weak calcium hypochlorite solution precipitates blue indigo, but an excess of the hypochlorite bleaches.

effervescence is over, add 200 c.cs. of water and boil, then filter rapidly and allow to cool. Isatine separates in small nodules on standing, as it is but slightly soluble in cold water, and more can be obtained on evaporation. By crystallisation from hot alcohol it can be obtained in fine brownish-red crystals. It performs rather an acidic part, and unites with the alkali metals. When dissolved in very strong caustic potash, it affords a fine deep violet solution. Isatine dissolves in strong sulphuric acid, and this solution is used as a test for *thiophene* in benzene (see p. 357).

By oxidation, then, indigo affords isatine ; on the other hand, when heated with zinc dust it yields *indole*, C_8H_7N. Between these extremes two other compounds are known, viz. *dioxindole*, $C_8H_7NO_2$, and *oxindole*, C_8H_7NO, which can be obtained by the action of nascent hydrogen on isatine. The relations of these compounds to indigo and to each other are shown in the following diagram :—

$$\text{Indigo, } C_8H_5NO \begin{cases} C_8H_5NO_2, & \text{isatine} \\ C_8H_7NO_2, & \text{dioxindole} \\ C_8H_7NO, & \text{oxindole} \\ C_8H_7N, & \text{indole} \end{cases}$$
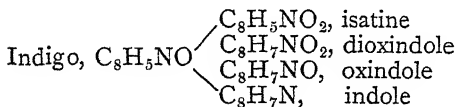
Indigo derivatives are met with in man. *Indican* is often present in urine, and can be detected by heating with a little strong hydrochloric acid, which breaks up the glucoside, as during the fermentation in indigo vats, and the addition of a very minute trace of calcium hypochlorite solution develops the blue colour of indigo. *Indole* is formed during *pancreatic* digestion of albuminous compounds, and is found in

fæcal matter. Indole injected under the skin is oxidised and appears in the urine as blue indigo. It is probable that the colouring matter excreted by the skin round the eyes &c. in cases of *chromidrosis* is due to vicarious elimination of indican, or a derivative of it, as pointed out by Dr. A. W. Foot.

The hydrocarbides of the C_nH_{2n-10} series are the next in order. The only member of any immediate interest is the compound C_8H_6, which can be derived from styrene, C_8H_8, by conversion of the latter into the dibromide, $C_8H_8Br_2$, and subsequent treatment with potash—

$$C_8H_8Br_2 + 2KOH = C_8H_6 + 2KBr + 2H_2O.$$
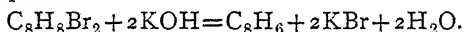
The new hydrocarbide bears the same relation to acetylene that styrene does to ethylene (see p. 326).

Acetylene .	. .	$H—C\equiv CH$
Phenyl-acetylene	.	$C_6H_5—C\equiv CH.$
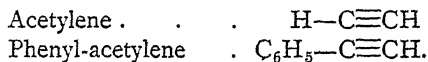
The latter is sometimes termed ' acetenyl-benzene,' and is regarded as the hydrocarbide from which indigo may be supposed to arise. The easy production of the blue colouring matter by reduction of propiolic (an acetylenic) acid is in accordance with this view.

The next series, C_nH_{2n-12}, is chiefly represented by the solid hydrocarbide *naphthalene*, $C_{10}H_8$, which is a common product of the action of strong heat on compounds relatively richer in hydrogen. It is present in considerable proportions in coal-tar, and is chiefly obtained from the products which distil about

218°, the boiling-point of naphthalene. But it vola-
tilises easily far below its boiling-point, and is therefore
found in most of the coal-tar products : this property
renders it a nuisance to gas companies, as it is carried
along with the coal-gas and deposited in the solid
form in the street mains, which it tends to plug. It
can be easily purified by sublimation : it melts at 79°.

Naphthalene resembles benzene in its stability
and action as if a saturated hydrocarbide. It affords
two monosubstituted derivatives by methods similar
to those used in the formation of ordinary benzene
compounds ; for example, two *bromonaphthalenes*,
$C_{10}H_7Br$, *nitronaphthalenes*, $C_{10}H_7NO_2$, *amidonaph-
thalenes*,[1] or *naphthylamines*, $C_{10}H_7NH_2$, and *naph-
thols*, $C_{10}H_7OH$, or phenols. Why two of each are
formed will be presently explained. Metameric di-
and other derivatives are also known, and are very
numerous. The resemblance of naphthalene to ben-
zene is therefore strong, and leads to the conclusion
that the two hydrocarbides are similar in structure.
The simplest hypothesis as to the constitution is that
naphthalene results from the union of *two benzene rings*,
with the loss of two atoms of hydrogen, thus—
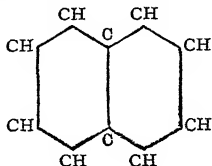
[1] These afford colours similar to those produced by aniline,
but with the exception of the yellows they are much less
brilliant.

And its chief relations above mentioned accord with this view and with the fact that it yields *phthalic acid* when oxidised, indicating that the union of carbons occurs in the *orthoposition* (see p. 297). Moreover, its recent synthesis from orthoxylene by Baeyer and W. H. Perkin, while confirming the evidence afforded by the production of phthalic acid, directly supports the double-ring hypothesis. They first converted orthoxylene at 125° into the side-chain bromide—

$$C_6H_4 \Big\langle \begin{matrix} CH_2\text{---}Br \\ CH_2\text{---}Br \end{matrix}$$
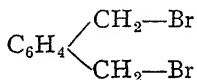
and replaced the bromine atoms by two residues of ethyl *malonate* (see page 174), which they succeeded in linking as shown—

$$C_6H_4 \Big\langle \begin{matrix} CH_2\text{---}C=(COOC_2H_5)_2 \\ \quad\quad | \\ CH_2\text{---}C=(COOC_2H_5)_2. \end{matrix}$$
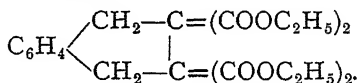
The carboxethyl groups were ultimately split off, and the residue—

$$C_6H_4 \Big\langle \begin{matrix} CH=CH \\ \quad | \\ CH=CH \end{matrix}$$
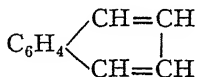
was *naphthalene.*[1]

The reason for the existence of *two* metameric *mono*-substituted naphthalene derivatives is not far to seek if the above structure of the hydrocarbide be granted. It is obvious that we may number the eight hydrogen atoms in naphthalene, just as in benzene,

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[1] Meta- and paraxylene do not afford double-ring compounds.

following the direction in which the hands of a watch move ; thus—
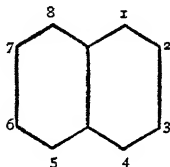
There are evidently *two* distinct sets of positions which are distinguished as the α and β positions. When an atom of hydrogen is replaced at any one of the points 1, 4, 5, or 8, an α compound is obtained ; but if at 2, 3, 6, or 7, a β compound.   In the direct attack of naphthalene *both* products are generally obtained ; thus when heated with sulphuric acid it affords α and β sulphonic acids, and these on fusion with potash yield corresponding α and β naphthols.   The α sulphonic acid, when strongly heated, passes into the β, which is the more stable variety.   The β naphthol now used in medicine is prepared by heating the hydrocarbide with strong sulphuric acid to 170° and fusing the product with potash.   The naphthol is then separated by treatment of the solution of the naphtholate with an acid.   It is interesting to compare these phenols as follows :—

α *Naphthol*, $C_{10}H_7OH$.—Small colourless needle-like crystals, slightly soluble in water, easily in alcohol.   Melts at 94° ; its b.p. is 278°. Coloured light *purple* by ferric chloride or calcium hypochlorite.

β *Naphthol*, $C_{10}H_7OH$.—Crystalline plates, mode-

rately soluble in hot water, easily in alcohol. Melts at 122°; its b.p. is 286°. Coloured greenish by ferric chloride and yellow by calcium hypochlorite.

The action of ammonia on naphthol is remarkable, as the *amido-compound*, $C_{10}H_7(NH_2)$, is formed.

Two quinones, $C_{10}H_6O_2$, are known, α and β, and are easily formed by direct oxidation of the hydrocarbide with chromic acid. The naphthaquinones are distinctly *ketonic* compounds and exhibit little of the *peroxide* character which is so marked in ordinary quinone.

The C_nH_{2n-14} series of hydrocarbides is represented by *diphenyl*, $C_{12}H_{10}$; *diphenylmethane*, $C_{13}H_{12}$; and *dibenzyl*, $C_{14}H_{14}$. These have been already referred to at pp. 301 and 323, as well as *stilbene*, $C_{14}H_{12}$, which belongs to the C_nH_{2n-16} series. These do not afford compounds of much interest.

CHAPTER LXVI.

ANTHRACENE AND PHENANTHRENE—THEIR SEPARA-
TION AND STRUCTURE—ANTHRACENE DERIVA-
TIVES—ANTHRAQUINONE—ALIZARINE AND OTHER
HYDROXYQUINONES—ARTIFICIAL ALIZARINE—PUR-
PURINES—THEIR MANUFACTURE. HIGHER SERIES
OF HYDROCARBIDES. BENZENOID CHARACTERS OF
TERPENES—COMMON TURPENTINE—BROMIDES—
HYDROCHLORATES—ARTIFICIAL CAMPHOR—CAM-
PHENES—ORDINARY CAMPHOR, ESSENTIAL OILS
—CITRENES—STEAROPTENES.

THE series of hydrocarbides whose general formula is C_nH_{2n-18}, includes *tolane* or diphenylacetylene, $C_{14}H_{10}$, which we have already seen (p. 323) can be derived from dibenzyl, and two remarkable metamers of it, viz. *anthracene* and *phenanthrene*. Of these anthracene is of chief importance, as it is the prime material employed in the manufacture of 'artificial alizarine,' which has now almost completely displaced the dyestuff of the same name obtained from the madder plant.

Anthracene is obtained from coal-tar and forms a considerable portion of the product which distils between 300° and 360°. Within that range of temperature a liquid is obtained which becomes on

cooling a greenish-yellow mass of the consistence of
butter : this is pressed to remove adherent oils, and
the solid is crude anthracene.   If this be washed
with cold benzene and again pressed, a sufficiently
pure product is obtained for most purposes ; but it
contains its metamer phenanthrene.   When dissolved
in boiling alcohol, and the solution cooled, nearly
pure anthracene crystallises out, but the phenanthrene
is much more soluble in alcohol, and is retained in
solution.   By evaporation of the latter, *phenanthrene*,
$C_{14}H_{10}$, separates, and can be purified by repeated
crystallisation from alcohol : it is then obtained in
pearly crystalline plates that melt, at 100°, to a liquid
which boils at 340°.   We shall refer again to this
hydrocarbide.

Anthracene, $C_{14}H_{10}$, is finally purified by sublima-
tion, and is generally purchased as 'sublimed anthra-
cene.'   So obtained it occurs in beautiful flat crystals
having a bluish fluorescence : it fuses at 213° and
boils about 360°.   It is slightly soluble in cold alcohol
and benzene, but is much more soluble in the hot
liquids.   It is soluble in boiling acetic acid.

Anthracene is produced by the action of heat on
many benzene compounds ; thus it is formed when
toluene is passed through a red-hot tube—

$$2(C_6H_5CH_3) \;=\; C_{12}H_{10}+6H$$
$$\underbrace{}_{\text{Toluene.}} \qquad \underbrace{\phantom{C_{12}H_{10}}}_{\text{Anthracene.}}$$

This mode of generation points to the presence of
two benzene residues in anthracene.   How these can
be linked is best shown by the formation of anthra-
cene by the action of acetylene tetrabromide on

benzene in presence of aluminum chloride, according to Friedel and Crafts' method—

$$C_6H_6 \quad CHBr_2$$
$$+ \quad | \quad = \quad C_6H_4 \Big\langle {}^{CH}_{CH} \Big\rangle C_6H_4 + 4HBr.$$
$$C_6H_6 \quad CHBr_2$$
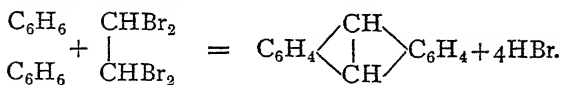
Thus the two benzene rings would appear to be doubly linked in the ortho-position by the $=CH—CH=$ group derived from acetylene, instead of being directly joined as in naphthalene ; thus—

Naphthalene. : Anthracene.
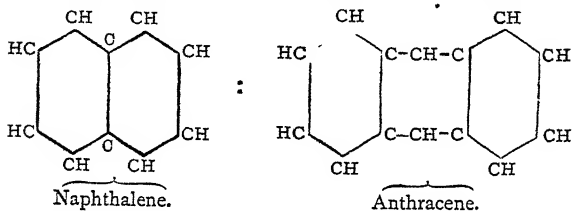
All the reactions of anthracene accord with such a structure. The metameric phenanthrene acts as if its structure were intermediate between that of naphthalene and anthracene, *i.e.* that it includes two benzene rings, also united in the ortho-position, but at one point *directly*, and at the other by a CH—CH loop or chain. We cannot enter into the chemical evidence on this point here, but it is noteworthy that photographs, taken by Hartley, of the spectrum of white light which has passed through a colourless solution of phenanthrene show five absorption bands in the ultra-violet portion, whereas anthracene and naphthalene similarly examined give only four bands, as do benzene and most of its recognised substitution compounds.

Anthracene unites readily with *two* monad-atoms

or groups; thus with two atoms of hydrogen it affords *dihydranthracene*, $C_{14}H_{12}$, and with picric acid a dipicrate, the addition in each case seeming to be to the linking CH groups.

Experiment 803.—Dissolve about a gram of anthracene with heat in the least possible quantity of benzene, prepare a similar hot solution of three grams of picric acid, and mix the two liquids. On cooling, fine crimson needles of *anthracene picrate*, $C_{14}H_{10}(C_6H_7N_3O_7)_2$ crystallise out. Phenanthrene treated in the same way gives a yellow picrate.

Nitro-derivatives of anthracene can be obtained, as well as phenols, termed *anthrols*: these are substitution products obtained by the replacement of hydrogen in the benzene rings. The direct action of nitric acid is, however, complicated, owing to the strong tendency of anthracene to form a *quinone* (see p. 288), so that nitro-quinones are obtained instead of nitro-derivatives alone. But when heated with *chromic acid* the possibility of forming a nitro-compound is of course excluded, and the quinone alone, or *anthraquinone*, is obtained. The latter bears the same relation to anthracene as ordinary quinone to benzene; thus—

Benzene . . C_6H_6 . . Quinone . . . $C_6H_4O_2$
Anthracene . $C_{14}H_{10}$ . . Anthraquinone $C_{14}H_8O_2$

The best mode of producing anthraquinone in small quantity is the following, which was originally recommended by Graebe and Liebermann, and is now used exactly as described in the estimation of anthracene in the crude hydrocarbide.

Experiment 804.—Pour into a 250 c.c. flask 25 c.cs. of glacial acetic acid, add five grams of nearly

pure anthracene, and boil. Connect the flask with a vertical condenser, and pour through the tube of the latter a solution of 7·5 grams of *chromic anhydride*,[1] in 20 c.cs. of a mixture of equal parts acetic acid and water. Not more than 2 c.cs. of this solution should be added to the boiling contents of the flask at intervals of three or four minutes. After finally boiling well allow the liquid to cool, fill up the flask with cold water, and let it stand for an hour. Anthraquinone is precipitated, as it is insoluble in water. It should be collected in a filter, washed with very dilute caustic soda solution, finally with pure water, and dried at 100°. Five grams of perfectly pure anthracene can afford in this way 5·8 grams of anthraquinone.

Anthraquinone can also be obtained, together with benzophenone, by heating *calcium phthalate*. As this mode of producing it is similar to that which affords *acetone*, we have genetic evidence that it is a diketone. The decomposition can obviously be represented as under :—

$$C_6H_4 \begin{array}{c} COO \\ COO \end{array} Ca \; + \; Ca \begin{array}{c} OOC \\ OOC \end{array} C_6H_4$$

$$\underbrace{\hspace{5cm}}_{\text{Calcium phthalate, 2 mols.}}$$

$$= \quad C_6H_4 \begin{array}{c} CO \\ CO \end{array} C_6H_4 \quad + 2CaCO_3$$
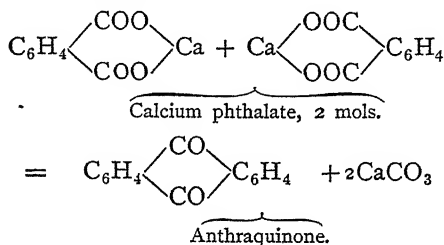
$$\underbrace{\hspace{3cm}}_{\text{Anthraquinone.}}$$

[1] If an impure anthracene be used, a much larger quantity of CrO_3 will be required to destroy the impurities. Potassium dichromate does not afford as satisfactory results as the acid.

Crude anthraquinone is easily purified by sublimation. It melts at $274°$, and affords a vapour which condenses in fine yellowish needles, generally felted together. The pure compound is almost completely insoluble in water, very slightly in cold alcohol or benzene, but is dissolved to some extent on boiling. It is very little prone either to oxidation or reduction ; but can afford bromo-derivatives and sulphonic acids, from which hydroxyanthraquinones can be obtained by fusion with potash. Some of these will presently be referred to, but we must now point out that anthraquinone when heated with zinc dust yields *anthracene*, and the alizarine of madder when treated in the same way affords the same hydrocarbide. The 'madder' plant, *Rubia tinctorium*, has long been cultivated in the East for the sake of its roots, which contain a *glucoside* termed ruberythric acid. The latter undergoes hydrolysis during the fermentation of the moist roots or the aqueous extract, with the separation of *alizarine* and glucose ; thus—

$$C_{26}H_{28}O_{14} \ + \ 2H_2O \ = \ C_{14}H_8O_4 \ + \ 2C_6H_{12}O_6$$

Ruberythric acid.   Alizarine.   Glucose.
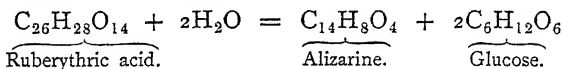
Alizarine is a crystalline body which affords magnificent red-coloured lakes with alum salts and those of tin, and has long been used by dyers for the production of the well-known 'Turkey red' cloths.

The knowledge of the apparently trivial fact that alizarine affords anthracene on heating with zinc dust proved in the hands of Graebe and Liebermann the key to the solution of a very important problem, namely, the synthesis of the dye. This they effected

in 1868, only six years after the late Dr. Anderson, of Glasgow, had fully established the composition of anthracene, which was regarded at that time as an uninteresting and useless hydrocarbide.

A comparison of the formulæ of anthracene, anthraquinone, and alizarine indicates their *general* relations :—

$$C_{14}H_{10} \quad : \quad C_{14}H_8O_2 \quad : \quad C_{14}H_8O_4$$

Anthracene.   Anthraquinone.   Alizarine.
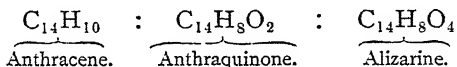
Now, since the number of atoms of hydrogen in the quinone and alizarine is the same, though the latter contains two atoms more of oxygen, there is a strong presumption in favour of the view that alizarine is a dihydroxyanthraquinone ; thus—

$$C_{14}H_8O_2 \quad : \quad C_{14}H_6(OH)_2O_2.$$

Graebe and Liebermann soon showed that this view is correct, and succeeded in converting the quinone into alizarine by a method that we shall now follow on a very small scale.

Experiment 805.—Make an intimate mixture of one gram of anthraquinone with rather less than half its weight of powdered iodine, and pass the mixture down to the closed end of a long and rather narrow tube (40 c. ms. long by 1 c. m. in diameter). Now drop in 1 c.c. of bromine. Support the tube by a clip so that the end shall dip a few centimeters under water boiling in a beaker, and near to a good draught. Heat in this way for an hour. The long tube acts to some extent as a condenser for bromine that distils up and then returns to the solid. Finally remove

from the water, and heat the contents of the tube to about 160° over a gas flame until most of the brown colour has disappeared, then let the contents cool. During this treatment some mono- and di-bromo-anthraquinones are formed. To convert the product into alizarine put the solid residue into a small thin porcelain capsule, rub the solid with enough solution of caustic potash to remove the colour of bromine and iodine, and then throw in a small lump of solid caustic potash, boil down to dryness, and heat the residue to about 200°. It gradually assumes a blue or purple shade, owing to the formation of a little alizarine (or its potassium compound); when the shade no longer deepens allow to cool, and add water; then a purple solution of alizarine in caustic potash is obtained. If the tint be deep, add water and filter into some diluted hydrochloric acid, when a brownish-yellow precipitate of alizarine will fall. But with the small quantities used above it is scarcely worth while to adopt this treatment unless the experiment has been very successful throughout. There is no difficulty about getting a strong colour. The change on fusion is—

$$C_{14}H_6Br_2O_2 + 2KOH = C_{14}H_6(OH)_2O_2 + 2KBr.$$

Dibromanthraquinone.   Alizarine.
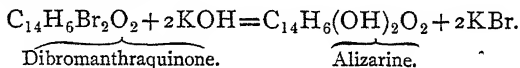
This is the usual phenolic reaction. On the large scale the anthraquinone is heated with fuming sulphuric acid very rich in anhydride, when mono- and di-sulphonic acids are formed. The product, after dilution with water, is mixed with calcium chloride, calcium sulphate and unused anthraquinone

are filtered off, the necessary excess of caustic soda is added, the liquid evaporated to dryness, and the product fused until the maximum quantity of alizarine is produced. On solution in water and precipitation by excess of acid, the crude alizarine is obtained. This, when dry, can be sublimed, and affords orange-red needles of the compound.

Alizarine acts as a phenol, and affords soluble phenolates of the alkalies, which are purple-coloured, and from which the red alumina and tin lakes already referred to can be precipitated.   .

Alizarine from madder always contains a tri-hydroxyanthraquinone named *purpurine*; artificial alizarine also contains that body and substances metameric with the last-named, *anthrapurpurine* and *flavopurpurine*, which can be separated and are as valuable as alizarine itself.

The following formulæ are given for these bodies on the authority of Mr. W. H. Perkin, who has done as much for the development of the alizarine industry as for that of the aniline dyes :—

Alizarine[1] . . . $C_6H_4 \begin{matrix} CO \\ CO \end{matrix} C_6H_2 \begin{matrix} OH^{(1)} \\ OH^{(2)} \end{matrix}$

Purpurine . . . $C_6H_4 \begin{matrix} CO \\ CO \end{matrix} C_6H \begin{matrix} OH^{(1)} \\ OH^{(2)} \\ OH^{(4)} \end{matrix}$
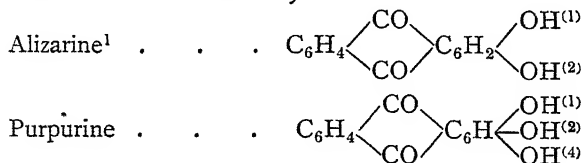
[1] The small figures or letters in brackets indicate positions I : 2 or I : 2 : 4. Baeyer has shown that the two hydroxyls of alizarine are in the ortho position in one ring by producing alizarine from phthalic anhydride and *pyrocatechine*. Anthra-flavic acid is a metamer of alizarine with the hydroxyls in different rings.

Anthra-purpurine[m] HO—C_6H_3 $\big\langle^{CO}_{CO}\big\rangle$ $C_6H_2\big\langle^{OH[1]}_{OH[2]}$

Flavo-purpurine [o] HO—C_6H_3 $\big\langle^{CO}_{CO}\big\rangle$ $C_6H_2\big\langle^{OH[1]}_{OH[2]}$
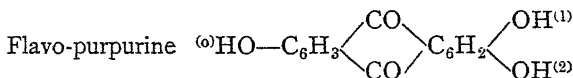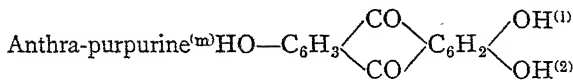
It would not serve any useful purpose to continue the enquiry further in this direction at present.

By Graebe and Liebermann's important discovery the foundation was laid of a great industry ; how great a one will appear when it is stated that the average annual crop of madder roots prior to 1869 was 70,000 tons, valued at 3,150,000*l.* sterling ; but now the plant is scarcely grown. On the other hand much more than the equivalent of artificial alizarine is manufactured, and in doing so an otherwise waste product, anthracene, is utilised.

It does not come within the scope of the present work to refer to the little-known hydrocarbides of the higher series up to C_nH_{2n-40} ; but there yet remains for brief notice the remarkable group of *terpenes* before we reach the final stage of our course.

The natural group of turpentines or *terpenes* are the only important [1] members of the C_nH_{2n-4} series of hydrocarbides. They are metamers of the formula $C_{10}H_{16}$, and all probably contain a benzene nucleus ; their consideration has therefore been deferred until now, in order that their obscure benzenoid character may be appreciated.

[1] Valylene, C_5H_6, is the lowest known term of the series.

Although terpenes are found in most of the essential or volatile oils distilled in a current of steam from various plants, such as lavender, bergamot, mint, thyme, &c., the common 'oil' or spirit of turpentine used by painters is the most convenient type of the class, and as such we shall use it.

Common 'oil of turpentine' is derived from the oleo-resinous exudation of the varieties of the pine tribe. This material is represented by the pasty 'Venice turpentine' met with in commerce. The French turpentine is chiefly obtained from *Pinus maritima*, and the American or 'English' oil from *Pinus australis*. The crude exudation is distilled with water, or steam is blown through it, when the oil or spirit passes over with the vapour of water and forms a layer on the surface of the condensed liquid. A residue is left in the retort which solidifies to a hard, brittle mass on cooling : this is common *rosin*, or resin used for varnishes, &c. The latter is a mixture of feeble acids, and, when boiled with caustic alkalies, forms a kind of *soap*. Most of the cheaper brown soaps contain considerable proportions of saponified resin.

Oil of turpentine, $C_{10}H_{16}$, is a colourless, mobile liquid having a strong and unpleasant smell, which varies somewhat with the source. Its boiling-point is 156°, and its sp. gr. varies from 0·86 to 0·88. It does not mix with water, but is easily miscible with alcohol and ether. The French and American oils do not act in the same way on polarised light, the former being *lævogyrate*, and the American variety *dextrogyrate*.

Experiment 806.—Moisten a strip of dried white bibulous paper with a few drops of turpentine, and plunge into a jar of chlorine gas. The liquid quickly takes fire and carbon separates, while fumes of hydrochloric acid are developed. This violent disruption of turpentine is in contrast with the action of chlorine on benzene under similar conditions.

Bromine also acts very energetically at ordinary temperatures, but when cooled to —20 terpene affords addition compounds, viz. *terpene dibromide,* $C_{10}H_{16}Br_2$, and *tetrabromide,* $C_{10}H_{16}Br_4$. The former readily loses 2HBr, and there results *cymene,* $C_{10}H_{14}$, which is paramethylpropyl benzene.

Nitric acid, when strong, acts so violently as to inflame turpentine ; when diluted with water it produces *terephthalic acid,* $C_6H_4(COOH)_2$ (see p. 296), which, like cymene, is a para-derivative of benzene. If, however, turpentine be allowed to stand with one-third of its volume of a mixture of equal parts colourless nitric acid, water, and alcohol, crystals of a trihydrate separate, and these afford the monohydrate or *terpin* when dried at 100°.

The action of hydrochloric acid is remarkable.

Experiment 807.—Place in a flask surrounded by cold water 100 c.cs. of turpentine, and pass into it dry hydrochloric acid gas evolved from 100 grams of common salt.

The gas is quickly absorbed at first, and heat is evolved ; but the temperature of the turpentine must not be allowed to rise above 35°. As the absorption diminishes—and it is well to pass the gas slowly at the end—the external water should be

warmed to 35°,[1] by the addition of sufficient hot water. When there is no further absorption allow the liquid to stand. On cooling crystals of *terpene hydrochlorate*, $C_{10}H_{16}HCl$, separate out ; these can be drained from the liquid and recrystallised from alcohol. The mother liquor from the crystals is a metameric liquid hydrochlorate. By prolonged contact with fuming hydrochloric acid turpentine affords a dihydrochlorate from which a metamer of terpene named *terpilene* boiling at 176° is obtained by the action of heat.

The crystalline hydrochlorate is often termed *artificial camphor* ; it is readily distinguished from ordinary camphor, $C_{10}H_{16}O$, by evolving hydrochloric acid when burned. On heating with alcoholic potash hydrochloric acid is eliminated from the solid hydrochloride, and another metamer of terpene is obtained, which is termed *camphene*, $C_{10}H_{16}$: this is a solid which melts at 146°. When oxidised, camphene forms $C_{10}H_{16}O$, which agrees in properties with common camphor.

Natural *camphor* is obtained by distilling the wood of the *camphor laurel* with water, when the terpene oxide, or hydroxide, $C_{10}H_{16}O$, sublimes.

It is a white translucent crystalline solid, which is powdered with difficulty unless slightly moistened with alcohol. It has a powerful and agreeable odour, and a pungent taste. It floats on water, in which it dissolves to a small extent ; it is easily soluble in spirit of wine, ether, and chloroform. It readily sublimes and volatilises slowly even at ordinary temperatures.

[1] Berthelot finds that the maximum yield of solid hydrochlorate is obtained at this temperature.

When heated with dehydrating agents such as phosphoric anhydride, camphor affords nearly pure *cymene*.

Borneo camphor contains $C_{10}H_{18}O$. Little is really known of the constitution of any of these compounds save that they contain a benzene nucleus. Ordinary camphor and Borneo camphor seem to be related as a ketone to a secondary alcohol.

The essential or volatile oils distilled along with the vapour of water from certain plants such as lavender, bergamot, mint, and many other, include either terpenes which boil at 156° or metameric hydrocarbides which boil at 176°, and are distinguished as *citrenes*, because the essential oils derived from members of the *Citrus*—lime and lemon—family generally contain the hydrocarbide of higher boiling point. The citrenes afford dihydrochlorates most readily.

The citrenes are often accompanied in the oils by camphors or *stearoptenes*, which separate when the oil is cooled. In this way *thymol* separates from oil of thyme, *menthol* from that of peppermint, and *apiol* from parsley oil.

Thus the general group of terpenes is remarkable for the number of metamers it includes, all of which are readily attacked by bromine and nitric acid, and combine with hydrochloric acid to form solid or liquid compounds.

CHAPTER LXVII. AND LAST.

THE immense development of the chemistry of the aromatic compounds which has taken place of late years dates from 1865, when Kekulé proposed his celebrated 'benzene theory,' as already explained. The rapid adoption of his ring formula for benzene as a working hypothesis reduced to order great groups of compounds whose relations were otherwise unintelligible, and it is not too much to say that it has hitherto withstood the most careful investigation and keenest criticism.   Nevertheless the student must not suppose that chemists imagine such compounds as benzene and its derivatives to be rigid rings of carbon atoms arranged in the same plane.   What is really meant is that the atoms of which the benzene mole-

A A 2

cule consists are symmetrically disposed in space, and that they tend to retain the relative disposition, notwithstanding their constant intra-molecular motion, which is more probably rectilinear than circular in character. This at least is Kekulé's own view, and if others are disposed to form more rigid and less justifiable conceptions, blame does not apply to the distinguished inventor of the hypothesis or to others who use it in a scientific manner.

The success of the carbon-ring hypothesis naturally led chemists to look for 'rings,' including other elements as well as carbon, and several such compounds were soon recognised. We shall now very briefly notice a few of these by way of introduction to the study of the last group of compounds we shall deal with.

A liquid has been separated from amongst the products of the destructive distillation of pine wood, which boils at 32°. It is represented by the formula C_4H_4O, and was named *tetraphenol*[1] by Limpricht, who discovered it in the first instance amongst the products of the destructive distillation of mucic acid (see p. 240). The latter is a common product of the oxidation of several of the carbohydrates.

It has been shown that Limpricht's compound is neither a phenol, alcohol, ether, aldehyde, nor ketone ; consequently Baeyer regards it as containing a carboxygen ring, and he has named it *furfuran*, representing its structure as under. A compound has long been known termed *furfurol*, $C_5H_4O_2$: this is obtained

[1] This must not be confounded with the *creosote* of wood-tar, which is a mixture of phenols and hydrocarbides.

when a mixture of *bran* and an equal weight of sulphuric acid previously diluted with three volumes of water is distilled. Furfurol is an oily liquid, which boils at 160° and exhibits all the characters of an aldehyde. It seems to be related to furfuran somewhat as benzyl aldehyde is to benzene; thus—

$$
\begin{array}{ccc}
\mathrm{HC-CH} & & \mathrm{HC-CH} \\
\| \quad \| & & \| \quad \| \\
\mathrm{HC \quad CH} & : & \mathrm{HC \quad C-COH} \\
\diagdown \diagup & & \diagdown \diagup \\
\mathrm{O} & & \mathrm{O} \\
\text{Furfuran.} & & \text{Furfurol.}
\end{array}
$$
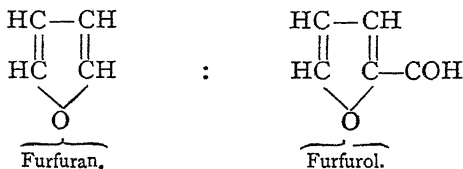
A compound analogous to furfuran, but containing sulphur instead of oxygen, has recently been separated from coal-tar benzene by Professor Victor Meyer, who has named it *thiophene*—

$$
\begin{array}{cc}
\mathrm{HC-CH} & \mathrm{HC-CH} \\
\| \quad \| & \| \quad \| \\
\mathrm{HC \quad CH} & \mathrm{HC \quad CH} \\
\diagdown \diagup & \diagdown \diagup \\
\mathrm{O} & \mathrm{S} \\
\text{Furfuran.} & \text{Thiophene.}
\end{array}
$$
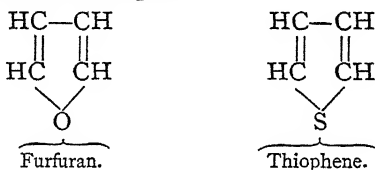
Thiophene was detected in benzene by shaking the latter with sulphuric acid containing some isatine (see p. 335) in solution. A fine *blue* colour is developed when thiophene is present; but benzene obtained by the destructive distillation of pure calcium benzoate does not afford this reaction. V. Meyer found that when benzene which affords the colour is shaken up with a little strong sulphuric acid the latter first attacks the thiophene forming a sulphonic acid,

and is so removed. From the sulphonic acid thiophene can be separated as a liquid which boils at 84°, and resembles benzene very closely in most of its characters.

We may obviously regard both furfuran and thiophene as products of the condensation of acetylene in presence of a little oxygen on the one hand, or sulphur on the other. The synthesis of furfuran has not yet been realised in any such way, but thiophene has been obtained by passing acetylene through boiling sulphur. In the destructive distillation of coal the small quantity of sulphur present .probably interposes in the production of benzene, and a little thiophene results.

When such elements as oxygen and sulphur can enter into a ' ring,' it is not surprising that compounds can be recognised in which *nitrogen* plays a similar part and confers somewhat basic properties on the compounds. Such substances have been recognised amongst the coal-tar products, but they are much more freely obtained from the oily liquid ('Dippel's oil'), produced when bones or other substances rich in nitrogenised organic matter are subjected to destructive distillation. A feebly basic liquid named *pyrrol*,[1] C_4H_5N, which boils at 130°, can be separated from the oil; and a more powerfully basic substance termed pyridine, C_5H_5N, which boils at 117°. The benzene-like characters of the former are not as strongly marked as are those of the latter, whose nature was first distinctly recognised by Professor Dewar. Pyrrol

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[1] It is noteworthy here that pyrrol is obtained by heating succinimide (see p. 192) with zinc dust.

is analogous to furfuran, whereas pyridine may be regarded as benzene which contains one atom of triad nitrogen instead of a triad CH group. These analogies appear from the following formulæ :—

$$
\begin{array}{c}
\text{HC—CH} \\
\| \quad \| \\
\text{HC} \quad \text{CH} \\
\diagdown\diagup \\
\text{NH}
\end{array}
$$

Pyrrol.

$$
\begin{array}{c}
\text{CH} \\
\diagup\diagdown \\
\text{HC} \quad \text{CH} \\
\| \quad \| \\
\text{HC} \quad \text{CH} \\
\diagdown\diagup \\
\text{N}
\end{array}
$$
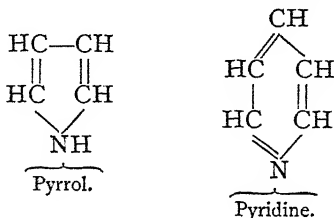
Pyridine.

Substituted pyridines are met with in bone oil, viz. methyl-pyridine or *picoline*, $C_5H_4(CH_3)N$; dimethyl-pyridine or *lutidine*, $C_5H_3(CH_3)_2N$; and trimethyl-pyridine or *collidine*, $C_5H_2(CH_3)_3N$.

The chief interest attaching to pyridine is that it appears to stand in nearly the same relation to the important class of vegetable alkaloids (nicotine, conine, strychnia, quinia, &c.) as benzene does to the aromatic compounds already dealt with.[1]   Most alkaloids afford on destructive distillation either pyridine or another basic compound termed *quinoline*, C_9H_7N, or *chinoline* (because obtained on heating cinchonine with potash). This substance was shown to be related to benzene by Professor Dewar, who obtained aniline from it. But Skraup was the first to effect its synthesis, which he did by heating aniline with glycerine and sulphuric acid, together with nitro-benzene, which acts

[1] Ladenburg has converted pyridine, C_5H_5N, into *piperidene*, $C_5H_{11}N$ (derived from the piperine of black pepper), by the action of hydrogen produced by sodium amalgam and water.

as an oxidising agent, and large quantities are now manufactured by this method—

$$C_6H_5NH_2 + C_3H_5(OH)_3 + O = C_9H_7N + 4H_2O.$$
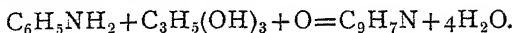
Quinoline is a liquid which is colourless at first, but quickly becomes brown on exposure to the air or to light. It boils at 236°. Skraup's synthesis is consistent with the view that quinoline is related to pyridine somewhat as *naphthalene* (see p. 338) is to benzene; thus—

Pyridine.   Quinoline.
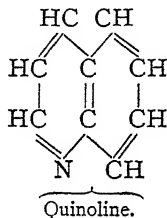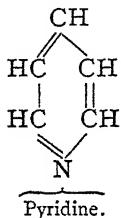
Quinoline is, like pyridine, the first member of a small series of homologues, viz. methyl-quinoline or *lepidine*, $C_9H_6(CH_3)N$, and dimethyl-quinoline or *cryptidine*, $C_9H_5(CH_3)_2N$.

An analogue of *anthracene* (see p. 343) is known named *acridine* in which one of the linking CH groups is replaced by an atom of nitrogen.

It is not desirable to follow up this subject more closely at this stage, but as we shall now notice the vegetable alkaloids of chief practical interest we shall point out any advances recently made towards a knowledge of their relations to the foregoing compounds.

Our space does not admit of detailed accounts of the mode of separating the basic nitrogenised substances termed 'alkaloids' from their natural sources. We shall therefore shortly state the essential features of each method [1] and confine our experiments to necessary tests for the alkaloids, as all the latter of any importance can be easily obtained in small quantities for the purpose. It must be clearly borne in mind, however, that these active principles of plants are in most cases highly poisonous bodies, and too much care cannot be taken in handling them.

It may be premised that the vegetable alkaloids [2] below described and their salts are characterised as a class by the following reactions of their solutions :—

1. *Iodine dissolved in potassium iodide.*—All afford yellow or reddish-brown precipitates.

2. *Phosphomolybdic acid.* [3]—Yellow or brownish-yellow precipitates with all.

We shall consider first the two best known alkaloids which do *not* contain oxygen, namely, *Conine* from hemlock, and *Nicotine* from tobacco. Neither

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[1] Following as closely as possible the British Pharmacopœia in all essential points.

[2] Caffeine and theobromine are not included in this statement, nor are they commonly classed as alkaloids ; they are of very different structure (see p. 218).

[3] This reagent is prepared as follows. Precipitate common sodium phosphate solution by ammonium molybdate, filter, wash the precipitate, and dissolve it by boiling with solution of sodium carbonate. Evaporate to dryness and heat until all trace of ammonia has disappeared, then dissolve the residue in ten parts of water acidulated with nitric acid.

compound is of much practical importance at present, but the former is of interest as the first vegetable alkaloid whose synthesis has been effected.

Conine, $C_8H_{17}N$, is the highly poisonous active principle of *Conium maculatum*, or hemlock, and is obtained from the seeds. These are crushed and distilled with water containing some lime or caustic soda. Conine, being a volatile liquid, comes over along with the vapour of water. The distillate is neutralised by sulphuric acid, evaporated to dryness, and the conium sulphate extracted from the residue with alcohol. The sulphate when distilled with an alkali gives free conine as a colourless oily liquid of unpleasant smell. Its specific gravity is 0·88, and it boils at 167°. Solutions of conine are dextrogyrate. The reaction of the compound is alkaline, and it readily forms salts. The hydrochlorate is characterised by melting at 218°.

Hofmann has shown that conine, when heated with zinc dust, affords a basic substance, *conyrine*, $C_8H_{11}N$, which is related to conine in the same way that pyridine is to piperidene (see note, p. 359), and can reproduce conine by addition of six atoms of hydrogen. Further, conyrine was shown to be *iso-propyl pyridine*—

$$(CH_3)_2CHC_5H_4N.$$

Ladenburg succeeded in producing this compound by heating pyridine with isopropyl iodide (see p. 108), and a metamer from picoline or methyl pyridine. When this was treated with nascent hydrogen six atoms were fixed, and a basic compound was obtained,

which had the composition of conine and most of its physiological properties; but it was not optically active, and its hydrochlorate fused at 204° instead of 218° It therefore was not identical with conine. It occurred to Ladenburg that his synthetic base might be an inactive mixture of two optically opposed conines, just as racemic acid is a mixture of two optically opposed tartaric acids (see p. 182); he therefore converted his base into the tartrate and placed in the strong solution of the salt a minute crystal of the tartrate prepared from natural conine. The crystallisation of a salt was thus determined in quantity, and the conine separated from it was found to be optically *dextrogyrate*, to afford a hydrochlorate which fused at 216°, and to be in all other respects identical in properties with natural conine.

Nicotine, $C_{10}H_{14}N_2$, is obtained from the leaves of *Nicotiana tabacum*. These are exhausted with water, the solution is evaporated to a small bulk, calcium hydrate added to set free nicotine, and the mixture shaken up with ether. The latter dissolves the nicotine, which is left when the ether is slowly distilled off; the alkaloid itself can be distilled at 240° in an atmosphere of hydrogen. The free base is a colourless, strong-smelling liquid, which is lævogyrate.

Little is known of the structure of nicotine save that it probably includes two pyridine groups.

The remaining alkaloids are oxygenated compounds, and are most conveniently grouped as in the following pages :—

The *opium alkaloids* are very numerous (seven-

teen or eighteen), and are derived from the milky juice obtained when incisions are made in the unripe seed-pods of the white poppy, *Papaver somniferum*. The juice is partly dried by exposure to the air, and the residue then constitutes the brown semi-solid mass termed 'opium.' The powerful narcotic action of the latter is due to the alkaloids present in it. Although numerous, those whose formulæ appear in the following list only are of interest at present. Morphia (with its artificial derivative, *apomorphia*) and codeia are actually in use as drugs, and mentioned in the British Pharmacopœia ; consequently they are the only constituents we shall refer to in any detail.

Morphia	.	$C_{17}H_{19}NO_3$
Apomorphia	.	$C_{17}H_{17}NO_2$
Codeia	.	$C_{17}H_{18}(CH_3)NO_3$
Thebaia	.	$C_{17}H_{15}(OCH_3)_2NO$
Papaverine	.	$C_{15}H_5(CH_3)(OCH_3)_4N$
Narcotine	.	$C_{22}H_{23}NO_7$
Narceine	.	$C_{22}H_{29}NO_9$

These are all basic bodies, and occur in opium in union with *meconic acid*, $C_7H_4O_7$, sulphuric and, possibly, lactic acids. The pharmacopœial process for the preparation of morphia consists in precipitating a concentrated aqueous solution of opium with calcium chloride, whereby meconic and other acids are separated as calcium salts and filtered off,[1] while the alkaloids remain as hydrochlorates in solution. The latter

[1] Meconic acid is a tribasic acid, but generally acts as if dibasic. It can be separated from calcium meconate by diluted

is boiled with animal charcoal to remove colouring matter, as in Experiment 227, and the filtered liquid is precipitated by ammonia added in slight excess. Most of the *morphia* is thereby thrown down, and can be collected, washed with a little water, and crystallised from hot alcohol. The filtrate from morphia when boiled affords some more of the alkaloid, which is removed, and potash then added in excess. Codeine, papaverine, and narcotine are thrown down. The precipitate is dissolved in hydrochloric acid, and codeia hydrochlorate is easily crystallised out from the solution, while the other bases remain in the mother liquor. Codeia is separated from its salt by potash, and is then crystallised from ether.

Pure morphia crystallises in short prismatic crystals, which are slightly soluble in cold water, to which it communicates a very bitter taste. It dissolves easily in caustic soda or potash, but not in ammonia, and is soluble in ethyl alcohol and in amylic alcohol, but is nearly insoluble in ether and is little dissolved by chloroform. It has a distinct alkaline reaction, and readily forms salts, which, being generally soluble in water, are chiefly used for the administration of morphia as a powerful narcotic ; the hydrochlorate and acetate are simply formed by solution of the base in the respective acids.

Experiment 808.—Divide a little finely powdered

sulphuric acid. It is obtained in micaceous crystals on evaporation. The acid dissolves slightly in cold water, easily in alcohol. Its solution gives a fine *red* colour with ferric chloride, which is destroyed by hydrochloric acid, but not by mercuric chloride.

morphia in four parts on a porcelain plate. (*a*) Drop some strong nitric acid on the powder. Note that a fine *red* colour is produced, which is not changed to violet on addition of a few drops of solution of sodium thiosulphate (see Brucia, p. 371). (*b*) Dissolve in a few drops of sulphuric acid ; no colour change takes place, but on stirring with a rod slightly moistened with diluted *nitric acid* a *rose* colour is produced, changing to yellow. (*c*) Pour over the powder a few drops of *ferric chloride*, and stir ; a fine *dark-blue* colour is developed. (*d*) Moistened with solution of *iodic acid* becomes brownish owing to separation of iodine. These tests serve to distinguish morphia from other alkaloids.

When morphia is heated in sealed tubes with hydrochloric acid, the base loses a molecule of water, and *apomorphia hydrochlorate*, $C_{17}H_{17}NO_2HCl$, is obtained in small greyish-white acicular crystals, which become green on exposure to light and air. It is easily soluble in water, and sodium bicarbonate throws down a precipitate, which becomes greenish on standing ; when ether is added a purple solution is obtained. In the solid state it gives the morphia reaction with nitric acid, but affords a *deep-red* colour with ferric chloride. Apomorphia is chiefly used as an emetic.

Codeia, or methyl-morphia, occurs in colourless octahedral crystals, much more readily soluble in water than morphia : its solution is distinctly alkaline.

Experiment 809.—Divide the powdered base in small portions on a porcelain plate and note that (*a*) nitric acid gives a *yellow* colour, not red like

morphia ; (*b*) dissolves without colour in strong sulphuric acid, but the solution stirred with a glass rod moistened either with diluted nitric acid or ferric chloride affords a *blue* colour, especially if warm. Codeia is a very weak narcotic, its chief sedative effect being exerted on the digestive tract. It is of special value in controlling the excretion of sugar in diabetes.

When codeia is heated under pressure with hydrochloric acid, it is stated to afford apomorphia, methyl chloride, and water ; hence the base is regarded as methyl-morphia. This conclusion has been confirmed by Grimaux's production of codeia by heating morphia with methyl iodide and sodium hydrate. There is some reason to believe that morphia itself is a derivative of *phenanthrene* (see p. 342).

Connected with the opium bases, by reason of some of their physiological properties and similarity as monazo-compounds, are the following alkaloids, viz:—

Atropia, $C_{17}H_{23}NO_3$, is extracted from the root of *Atropa Belladonna* by alcohol. When slaked lime is added, the base is set free ; the solution is then filtered, and diluted sulphuric acid is added to it ; the alcohol is then distilled off. The residue is treated with excess of sodium carbonate and shaken up with chloroform. The latter dissolves the alkaloid, and yields it on evaporation in crystals : these dissolve in water and afford an alkaline liquid, which gives a *citron yellow* precipitated with auric chloride solution. This alkaloid is a very powerful poison, but its chief use is in dilating the pupil of the eye.

Atropia is resolved by the action of water into *tropic acid*, which is related in the following way to

Hydroxypropionic acid . $CH_2OH—CH_2—COOH$
Tropic acid . . $CH_2OH—CH(C_6H_5)—COOH$
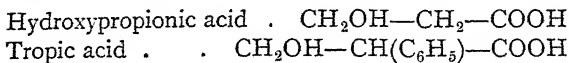
and *tropine*, $C_{18}H_{15}NO$, which appears to be a pyridine derivative.

Hyoscyamia, or hyoscyamine, the active principle of 'henbane,' or *Hyoscyamus niger*, is probably metameric with atropia, and similar in constitution.

Aconitia, $C_{33}H_{43}NO_{12}$, is the intensely poisonous crystalline alkaloid extracted from the roots of *Aconitum Napellus* by alcohol. The spirit is distilled off, and the alkaloid, precipitated from the residue by sodium carbonate, is dissolved when the mixture is shaken up with ether. The solution affords the base on evaporation. When a little is rubbed on the skin, it causes a tingling sensation followed by prolonged numbness. No satisfactory *chemical test* is known for this alkaloid.

Cocaine, $C_{17}H_{21}NO_4$, is obtained by the same kind of treatment as for aconitia, applied to the leaves of *Erythroxylon Coca*. Its hydrochlorate, which is a crystalline powder, is easily soluble in water, alcohol, and ether. The aqueous solution gives a yellow·precipitate with auric chloride, and a white precipitate with ammonium carbonate soluble in excess. The aqueous solution dilates the pupil of the eye like atropia, and, like aconitia, when applied to the tongue causes a tingling sensation followed by numbness and loss of taste, so that sugar cannot be distinguished

from salt. In consequence of this property of suspending sensation it is a valuable local anæsthetic.

Veratria, $C_{32}H_{49}NO_9$, the alkaloid of *cevadilla* and of *Veratrum album* ; extracted with alcohol and precipitated by ammonia. It is purified by resolution in hydrochloric acid and decoloration by animal charcoal ; the base is then reprecipitated by ammonia. It is a powerful poison ; locally applied with fatty matter it destroys sensation like atropia and causes tingling. A trace of the powdered alkaloid, when sniffed with the nostrils, causes violent sneezing.

Experiment 810.—Place a little of the powdered alkaloid on a porcelain plate and pour a few drops of strong sulphuric acid over it ; note that a brownish solution is obtained which on standing for *some minutes* changes to a magnificent *purple-red* colour.

The remaining alkaloids are all diazotic and are of two classes, one the *strychnos*, or 'convulsive,' the other the *cinchona*, or 'febrifuge' group.

The *strychnos alkaloids* are *strychnia* and *brucia*. They are both met with in the seeds of *Strychnos nux vomica* and in St. Ignatius' beans, combined with *igasuric acid*.[1] The alcoholic solution of the seeds is distilled and the residual liquid mixed with lead acetate to separate acids, &c. as insoluble lead salts. The alkaloids are left in solution, from which they are precipitated by ammonia. The precipitate is digested with alcohol, filtered, and the solution is evaporated to a small bulk, when strychnia separates out in crystals. The mother liquor contains the *brucia*, which can be obtained on further evaporation.

[1] A tannin-like compound coloured greenish by iron salts.

Strychnia, $C_{21}H_{22}N_2O_2$, occurs in colourless octa-hedrons. It is very slightly soluble in water, to which, however, it communicates an intensely bitter taste. It is easily soluble in boiling rectified spirit, but slightly in absolute alcohol or in ether.

Experiment 811.—(*a*) Place some powdered strychnia on a porcelain plate, and add a few drops of strong sulphuric acid. The alkaloid dissolves without colour. Draw rapidly a small crystal of *potassium dichromate* through the drop ; a *fine purple streak* is produced, but the colour quickly fades : this is quite characteristic. Many other oxidising agents give the same reaction with strychnia, but the dichromate, when used as above, gives the strongest indications. (*b*) To another small quantity of the alkaloid add a few drops of strong nitric acid ; no colour is produced if strychnia be free from *brucia.*

When a solution of ammonium sulphide is added to an alcoholic solution of strychnia, fine red crystals slowly separate, which consist, according to Professor Hofmann, who discovered the compound, of

$$C_{21}H_{22}N_2O_2H_2S_3.$$
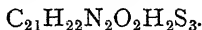
When treated with acids, oily drops of hydrogen per-sulphide are obtained. Other alkaloids do not afford such compounds.

We know little of the constitution of strychnia or brucia, save that the former readily acts like a tertiary ammonia and unites with methyl iodide, affording the *iodide* of *methyl-strychnium.* This compound has been shown by Professors Crum Brown and Fraser

to be in some degree antagonistic in physiological action to strychnia, and therefore capable of acting as an antidote, as curare does, in cases of strychnia poisoning.

Brucia, $C_{23}H_{26}N_2O_4$.—This alkaloid is like strychnia in appearance, in many of its physical properties, save that it is much more soluble in alcohol, and in its poisonous action. It is readily distinguished, however, as follows :—

Experiment 812.—Pour a few drops of nitric acid on some powdered brucia on a plate ; a fine *crimson-red* colour is produced (test for free nitric acid, see Experiment 100), rather like that given by morphia, but distinguished on addition of solution of sodium thiosulphate, which changes the red to a *violet* colour. Brucia is not coloured by sulphuric acid, and its solution in the latter does not react with potassium bichromate, nor is its aqueous solution coloured by ferric chloride.

The most interesting, probably the most valuable, of all the alkaloids are those derived from the bark of various *cinchonas* : these are chiefly *quinia, cinchonia,* and *cinchonidia* or *cinchonidine.* They are extracted from the powdered bark by diluted hydrochloric acid ; addition of ammonia in slight excess precipitates the alkaloids, which are then dissolved in just sufficient diluted sulphuric acid. The solution is decolorised by animal charcoal and evaporated to a small bulk when quinia sulphate crystallises out, while cinchonia and cinchonidia sulphates remain in the solution, along with *quinidine,* from which they can be afterwards obtained by successive crystallisations.

Quinia or *quinine* is generally met with in the form of the sulphate $(C_{20}H_{24}N_2O_2)_2H_2SO_47H_2O$, which is not easily soluble in water, but it is converted into a very soluble acid salt by the addition of diluted sulphuric acid. It forms a clear solution which is very bitter to the taste, and exhibits a beautiful *bluish fluorescence.* The solution is *lævogyrate.* Quinia and its salts do not afford characteristic colours with sulphuric or nitric acid ; but the following is a very characteristic reaction.

Experiment 813.—Dissolve a little quinia sulphate in water by the addition of a drop or two of hydrochloric acid, pour in a little fresh *chlorine* water, and immediately add excess of ammonia ; a fine *green* colour is at once developed.

Experiment 814.—Dissolve some quinia sulphate in warm acetic acid, and add to it in small quantities at a time an alcoholic solution of iodine. Beautiful thin plates, which are green by reflection, are slowly deposited. These consist of the compound $C_{20}H_{24}N_2O_2I_2H_2SO_45H_2O$. This is termed Herapath's salt, from its discoverer, or *artificial tourmaline,* because though they singly transmit white light the latter is polarised, and is stopped by a second crystal when superposed in certain positions. The crystals then act like ordinary tourmaline.

Cinchonia sulphate, $(C_{20}H_{24}N_2O)_2H_2SO_4,2H_2O$, is quite unlike the quinia salt in appearance, as it occurs in short prisms. It is soluble in water and in chloroform ; the aqueous solution is somewhat bitter to the taste, is *not* fluorescent when acidified, and is *dextrogyrate.* The base precipitated from the sul-

phate solution by ammonia is *not* dissolved by ether. Quinia similarly separated is soluble in ether ; hence the presence of cinchonia as an impurity of a quinia salt can be easily detected.

Cinchonidia sulphate is metameric with the foregoing, but its solution is lævogyrate, like that of quinine. Its acid solution is not fluorescent. Solution of the base readily affords a precipitate of its tartrate on addition of sodium tartrate solution.

The alkaloids are present in cinchona bark, chiefly as salts of *quinic* acid, $C_6H_7(OH)_4$—COOH, which is closely related to hexahydrobenzene, C_6H_{12}. Quinic acid is particularly interesting, because it was the original source of *quinone*, $C_6H_4O_2$, which is easily produced by its oxidation with manganese dioxide and sulphuric acid—

$$C_7H_{12}O_6 + 2O = C_6H_4O_2 + CO_2 + 4H_2O.$$
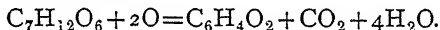
Experiment 815.—Boil 5 grams of powdered cinchona bark with 50 c.cs. of water, to which add a gram or so of slaked lime, filter and evaporate the filtrate to a small bulk in a porcelain capsule. When cool pour the residue into a test-tube containing about 2 grams of manganese dioxide, and add some sulphuric acid. The pungent smell of quinone is easily perceived, and in some cases a few golden yellow needles sublime on heating.

In quinic acid we have, then, a distinct benzene derivative, while quinia and cinchonia readily afford pyridine and quinoline derivatives; indeed the latter base derives its name from the fact that quinia when

distilled with caustic potash yields *quinoline.* All attempts to effect the synthesis of quinia have hitherto proved unsuccessful, though the economic importance of such a discovery would be great, as very large quantities of quinia and its related alkaloids are used as febrifuges.

The search for *quinia substitutes* has, however, been energetically carried on, and artificial quinoline prepared from aniline and glycerine by Skraup's process (see p. 359) was first pressed into the service, but it did not prove very successful in lowering temperature in fever cases. However, several derivatives of quinoline have proved of much greater value : of these *kairine* and *antipyrine* only have been much used, and need be noticed here.

The relations of *kairine* to quinoline and its tetra-hydride appear when the formulæ are written as under :—

$$\text{Quinoline} \quad \cdot \quad \cdot \quad \cdot \quad C_6H_4 \Big\langle \begin{matrix} N - CH \\ | \quad\quad \| \\ CH - CH \end{matrix}$$

$$\text{Quinoline tetrahydride} \quad C_6H_4 \Big\langle \begin{matrix} NH - CH_2 \\ | \\ CH_2 - CH_2 \end{matrix}$$

$$\text{Kairine} \quad \cdot \quad C_6H_3(OH) \Big\langle \begin{matrix} NCH_3 - CH_2 \\ | \\ CH_2 - CH_2 \end{matrix}$$
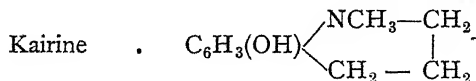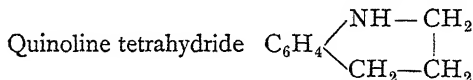
Commercial kairine is the hydrochlorate ; it has an extremely nauseous taste, which has been found to interfere very seriously with its utility. Antipyrine is not objectionable in this respect, and is now generally preferred to kairine. It is prepared by its discoverer,

Dr. Knorr, by the action of equal molecules of phenylhydrazine (see p. 276) on ethyl acetoacetate (see p. 165) ; water and alcohol are eliminated, and a compound termed *pyrazol*, $C_{10}H_{10}N_2O$, is formed. When treated with methyl iodide, methyl-pyrazol or *antipyrine* is formed, $C_{10}H_9(CH_3)N_2O$. This is a valuable agent in lowering temperature in febrile cases, especially in typhoid, but it is not an antiperiodic like quinia. It would appear from recent investigations that a much more simple benzene derivative, named *antifebrine*, but which is really *acetanilide* (see p. 272), is even more effective than antipyrine, and can be used in smaller doses. If further inquiry confirms this opinion, it is probable that the easily prepared acetanilide will displace antipyrine, just as the latter has pushed aside kairine. It is evident, then, that the study of the products of decomposition of the vegetable alkaloids has been fruitful in results of practical value, even though the synthesis of quinia itself has not yet been effected.

APPENDIX.

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THE ULTIMATE ANALYSIS OF ORGANIC COMPOUNDS.

THE great majority of organic substances consist of carbon, hydrogen, and oxygen only ; many others, as we have seen in the preceding pages, contain nitrogen, sulphur, and the halogens chlorine, bromine, and iodine ; while a much smaller proportion include phosphorus, arsenic, silicon, and the metals.

It would be out of place in the present work to describe in detail the various operations involved in the complete analysis of an organic compound, and the determination of its molecular weight. Such descriptions, to be of any real value, must be exceedingly minute, and would, moreover, be unintelligible without abundant illustrations : we have not space for either, and therefore refer the student for both to the special guides to Quantitative Analysis. The principles involved are, however, very simple, and are shortly stated in the following sketch of ultimate organic analysis, drawn up by my friend Dr. A. E. Dixon. Organic analysis obviously consists of two parts, viz. *qualitative* as well as *quantitative.*

QUALITATIVE ANALYSIS.

Detection of Carbon and Hydrogen.—The presence of carbon and hydrogen is best ascertained by heating to redness, in a hard glass tube, a mixture of the dry substance with recently ignited cupric oxide, a body

which readily parts with its oxygen. The products of combustion are passed, first, through a cold, dry tube, and, secondly, through lime-water. If the substance examined contain hydrogen, this is oxidised to water, which collects, in droplets, in the cold tube; while, if carbon be present, it is oxidised to carbon dioxide, whose presence is evidenced by the production of turbidity in the lime-water.

Detection of Nitrogen.—Nitrogen may, in many cases, be recognised by heating the substance with dry sodium hydrate, when ammonia is evolved. Certain nitrogenous substances, however, do not yield ammonia when thus treated; in such cases Lassaigne's test for nitrogen may be employed (see Pt. II. 4th ed. p. 199).

Detection of Sulphur.—There are numerous methods of recognising the presence of sulphur. The substance may be ignited with metallic sodium, and, after cooling, the residue is dissolved in water and added to a solution of sodium nitroprusside; a violet colour indicates sulphur (see Pt. II. p. 224). Or, the sulphur may be converted into sulphuric acid by boiling with nitric acid, and precipitated as barium sulphate.

Detection of Phosphorus.—The substance is heated in a sealed tube with HNO_3. If phosphorus be present, it is oxidised into phosphoric acid, which can be recognised by treatment with ammonium molybdate (see Pt. II. 4th ed. p. 270).

Detection of Haloid Elements.—A small fragment of pure copper oxide, attached to the end of a platinum wire, is heated to redness, allowed to cool somewhat, and then brought in contact with the substance. The fragment is now introduced into the outer flame of a Bunsen burner. A bright green colour is communicated to the flame if the smallest trace of chlorine, bromine, or iodine be present.

QUANTITATIVE ANALYSIS.

Quantitative Determination of Carbon and Hydrogen.—The principle on which the quantitative determination of carbon and hydrogen is based is as follows : all organic bodies, when burnt, under suitable conditions, evolve the whole of their hydrogen in the form of water, and their carbon in the form of carbon dioxide. A known weight of the solid substance to be analysed is accordingly mixed with some easily reducible metallic compound, such as CuO or $PbCrO_4$, and strongly heated. The water and carbon dioxide produced by the combustion are separately caught in suitable apparatus, and weighed. From the figures thus obtained the corresponding amounts of carbon and hydrogen are calculated, as 44 parts of CO_2 contain 12 of carbon, and 18 parts of water 2 of hydrogen. The process of 'combustion' is conducted in a glass tube of 50 or 60 cm. in length, in which the mixture of the substance with copper oxide is heated over a 'combustion furnace' by means of a row of Bunsen burners ; the aqueous vapour evolved is absorbed by calcium chloride, and the carbon dioxide by caustic potash.

If the substance to be analysed be a *liquid*, it is weighed out in a sealed glass bulb with a narrow stem ; the point of the latter is broken off and the bulb dropped into the combustion-tube.

If the substance contain *nitrogen*, a spiral of copper gauze is placed in the fore part of the tube and kept red-hot during the combustion : this is in order to decompose any oxides of nitrogen which may be formed, and which, if allowed to pass on, would be absorbed by the caustic potash, thus rendering the carbon determination too high.

If the substance contain chlorine, bromine, or iodine,

copper oxide cannot be used, since copper chloride, bromide, &c. would be formed : these bodies, being volatile, would pass on to the calcium chloride tube, and there condense. In this case lead chromate is employed instead of copper oxide, the lead chloride, &c. not being volatile. Lead chromate is also employed in dealing with bodies containing sulphur, since the latter, if burnt with CuO, evolve sulphur dioxide, which would be absorbed by the potash bulbs. Further, compounds of the alkali-metals, when burnt with CuO, leave a residue of carbonate ; in this case, also, lead chromate is used, which effects complete decomposition.

Quantitative Determination of Nitrogen.—Many nitrogenised compounds yield up the whole of their nitrogen in the form of ammonia, when heated with a solid mixture of caustic soda and slaked lime, termed 'soda-lime.' The ammonia, and consequently nitrogen, is determined by finding either the weight of *ammonium chloroplatinate* $(NH_4)_2PtCl_6$[1] it can afford, or the weight of dilute hydrochloric acid of known strength it can neutralise. This is known as *Will and Varrentrapp's method*, but it is inapplicable to compounds which contain nitrogen directly united with oxygen, *e.g.* nitroethane or nitrobenzene, as they do not yield up all their nitrogen in the form of ammonia. Such bodies are analysed by a method due to *Dumas*. This consists in burning a weighed quantity of the substance with oxide of copper in an atmosphere of carbon dioxide ; the whole of the nitrogen is obtained as gas ; any oxides of nitrogen that may be present are deoxidised by passing over red-hot copper gauze, and the gas is received in a measuring tube which contains caustic potash solution. The whole

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[1] Or the platinum left by ignition of this compound, since each atom of metal corresponds to two atoms of nitrogen.

of the nitrogen is swept into this measuring tube at the end of the combustion by a current of carbon dioxide, which latter is then absorbed out of the gaseous mixture by the caustic alkali. The weight of nitrogen is calculated from the volume so obtained, after correcting for temperature and pressure.

Quantitative Determination of Sulphur and Phosphorus.—These are estimated by heating in sealed tubes with fuming nitric acid, the sulphuric or phosphoric acid produced being precipitated as barium sulphate or ammoniaco-magnesian phosphate respectively.

Quantitative Determination of Chlorine, Bromine, and Iodine.—The weighed quantity of substance is heated in a narrow tube with pure caustic lime. After cooling, the contents are dissolved in dilute nitric acid, and the Cl, Br, or I precipitated by silver nitrate.

Determination of Oxygen.—Oxygen is generally estimated by difference : by subtracting the sum of the percentages of all the other elements present from 100, the difference represents the percentage of oxygen.

The composition of a substance having been determined, the empirical formula is deduced in the usual way (see Pt. I. p. 71). The question now arises, What multiple of this simplest formula represents the true, or molecular, formula? This can be answered when we have determined the molecular weight of the compound.

DETERMINATION OF MOLECULAR WEIGHT.

The most satisfactory determinations are those in which the compound is volatilised at a temperature well above its boiling-point and the specific gravity of its vapour, i.e. its *vapour density,* referred to hydrogen as the

standard. The vapour density, when doubled, gives the molecular weight (see Pt. I. p. 104), in accordance with Avogadro's law.

Thus the empirical formula of *acetone*, as deduced from its analysis, is C_3H_6O; the molecular weight should be 58. But its molecule might contain some multiple of C_3H_6O, such as $C_6H_{12}O_2$, in which case its molecular weight would be 116. Now the vapour density of acetone is 28·8; hence its molecular weight is $28·8 \times 2 = 57·6$. The question is therefore decided in favour of the formula C_3H_6O.

Again, the ultimate analysis of *benzene* leads to the empirical formula CH for that liquid, in which case its molecular weight should be 13. But its vapour density is 38·9; consequently its molecular weight is 77·8, or very nearly six times 13. Therefore the molecular formula of benzene is not CH, but C_6H_6.

FIG. 159.

The methods employed in such determinations are chiefly those of Hofmann and of Victor Meyer. In the former a weighed quantity of substance is introduced into a mercurial vacuum which can be raised to any required temperature short of the boiling-point of mercury. The volume of vapour obtained is then corrected to standard temperature, and, since its weight is known, it can be directly referred to the weight of the same volume of hydrogen under standard conditions.
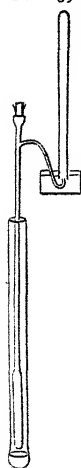
Victor Meyer's method is somewhat different in principle, and, being easier and quicker in practice, is now almost universally employed. It involves the use of the apparatus shown in the annexed sketch. The long glass bulb-tube is corked at the top, near to which point a side tube is sealed, which serves to deliver gas to the measuring vessel,

full of water, and standing in the little trough. The bulb-tube is full of air, which is heated to a constant temperature well above the boiling-point of the liquid whose vapour density is to be determined. This is accomplished, in the case of a liquid which boils below 100°, by immersing the bulb-tube in a steam-bath obtained by boiling water or other suitable liquid in the large outer glass tube. As the air expands on heating, it is allowed to escape without passing into the measuring tube ; but when no further change of volume occurs, a little bottle, containing a weighed quantity (0·1 to 0·3 gram) of the liquid under examination is dropped into the bulb, the cork having been removed for an instant for the purpose. The liquid is quickly converted into vapour, which latter expels its own volume of air into the measuring tube. The time occupied in doing this is less than a minute, so that no serious error from diffusion arises. The volume of air is corrected for temperature and pressure and its *weight* deduced. Finally, the *weight* of liquid taken, when divided by the *weight* of air expelled by the vapour at a constant temperature, gives the specific gravity of the *vapour* referred to air as the standard ; or, shortly—

$$\text{V. D.} = \frac{\text{Weight of Substance}}{\text{Weight of Air}}.$$

This value, when multiplied by 14·47, is the vapour density of the compound in terms of hydrogen.

When the compound is an *acid,* and its basicity is known, its silver salt is prepared and the percentage of silver determined in it. If the acid be monobasic, whatever weight of the compound is united with 108 parts of silver is the molecular weight *less* one atom of hydrogen replaced by silver. Thus, pure silver acetate was found

to contain 64·6 per cent. of silver, and the difference, 35·4 per cent., of acid radical ; consequently the weight of the latter united with 108 parts of silver is

$$\frac{34\cdot5 \times 108}{64\cdot6} = 59\cdot18.$$

59·18 + 1 = 60·18 is the molecular weight of the acid. The formula $C_2H_4O_2$ accords with the molecular weight = 60.

If the compound be basic, such as ethylamine, triethylamine, &c., advantage is taken of the fact that bodies of this class generally form chloroplatinates of the same type as the ammonium salt (see Pt. III. pp. 63 and 67), i.e. they contain two molecules of a monamine for one atom of platinum.

If the compound be anhydrous, a determination of platinum by simple ignition is the datum required. From the percentage of metal is then calculated that of H_2PtCl_6 in the compound, and from that, again, the weight of base in the molecule of the salt as in the case of the silver compound. The weight found, *divided by two*, is the required molecular weight, since there are two molecules of basic substance in the salt.

TEXT-BOOKS OF SCIENCE.

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